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# AMERICAN DYESTUFF REPORTER

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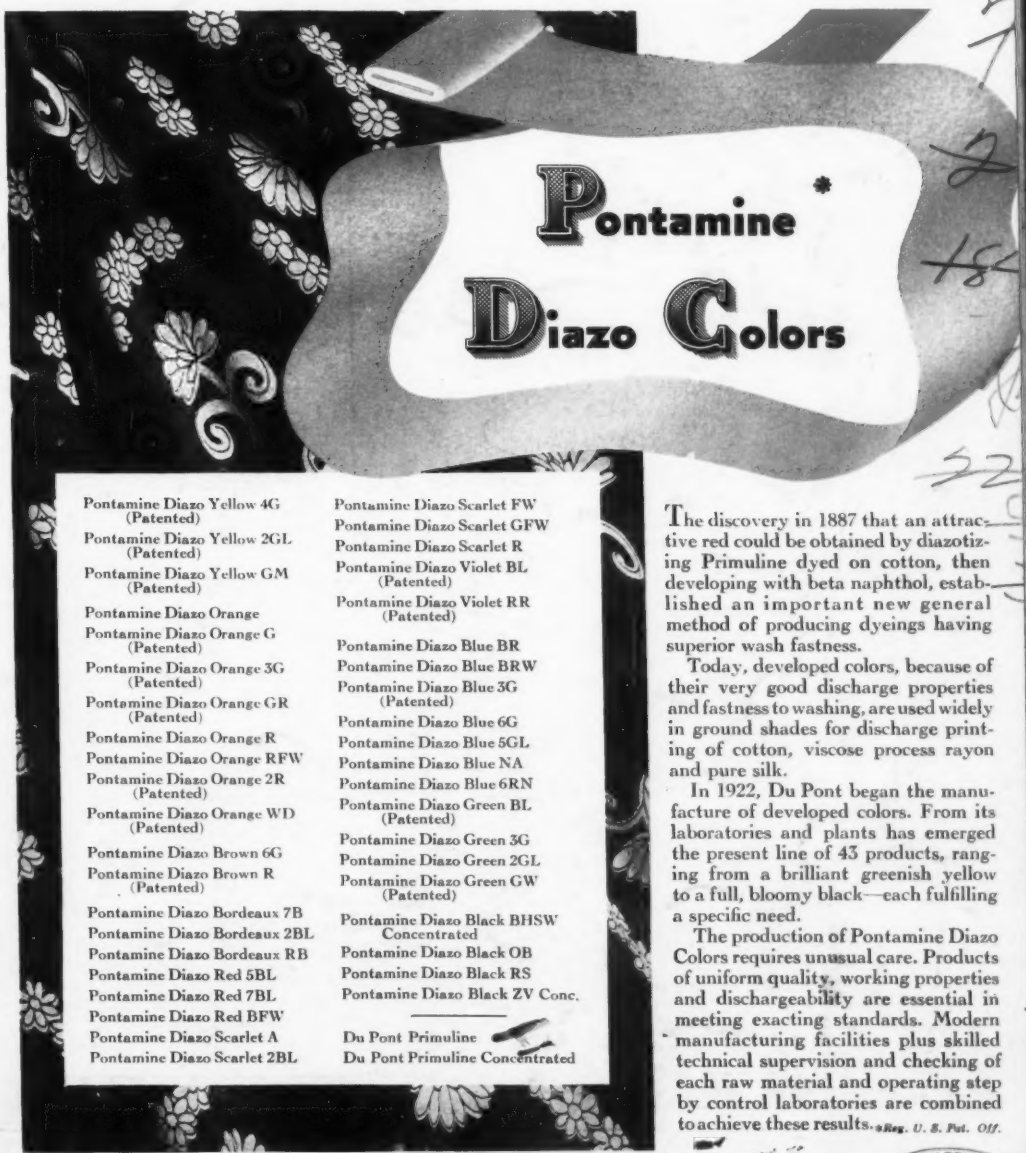


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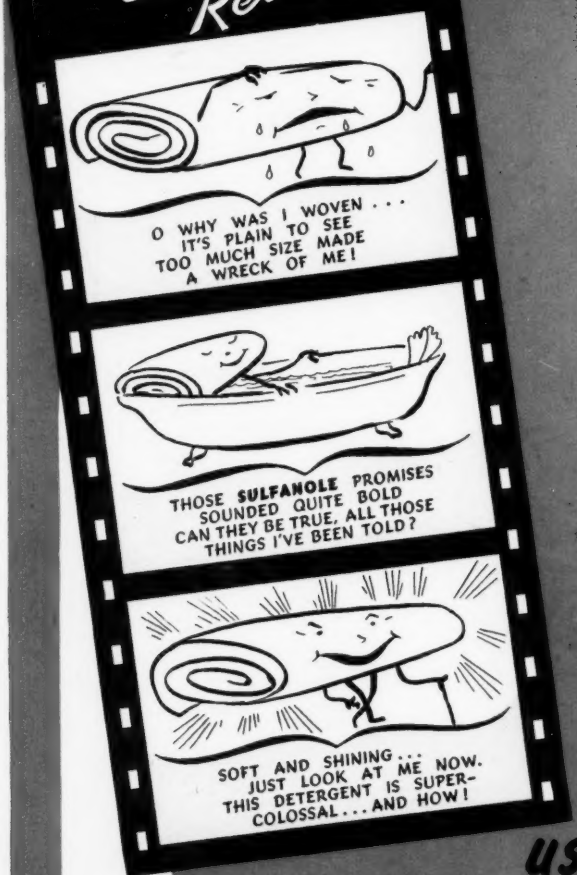
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# AMERICAN DYESTUFF REPORTER

A. P. HOWES
**Publisher**

LOUIS A. OLNEY
**Directing Editor**

NORMAN A. JOHNSON
**Managing Editor**

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Official Publication of the Proceedings of the American Association of Textile Chemists and Colorists

**MARCH 4, 1940**

**VOLUME 29 NUMBER 5**

American Dyestuff Reporter, Vol. 29, No. 5, Mar. 4, 1940. Published every other Monday. Copyright, 1940, by Howes Publishing Co., 440 4th Ave., New York, N. Y. Domestic subscription, $5.00, Canadian, $6.00, Foreign, $6.00. Entered as second-class matter, Nov. 6, 1919, at the New York, N. Y., Post Office, under the act of March 3, 1879.


## Contents

Contents of previous issues can be found by consulting the Industrial Arts Index at your library

### • Special Articles


Combination of Wool Protein with Acid and Base: Hydrochloric Acid and Potassium Hydroxide..... 103
Jacinto Steinhardt and Milton Harris


### • Departments


Technical Notes from Foreign Sources..... 108

Trade Notes—New Products..... 127

Open Forum ..... 129


### • Proceedings of the American Association of Textile Chemists and Colorists


Calendar of Coming Events..... P109

Three-Phase Light Sources of Interest to the Textile Industry as Applied to Accelerated Light Fastness Testing Equipment and Color Matching Lamps..... P110
Dr. M. J. Dorcas

Vinyon—A New Textile Fiber..... P116
Dr. F. Bonnet



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VOLUME 29 MARCH 4, 1940 NUMBER 5

# Combination of Wool Protein with Acid and Base:

## *Hydrochloric Acid and Potassium Hydroxide**

JACINTO STEINHARDT and MILTON HARRIS**

ABSTRACT

The protein material of which wool is principally composed possesses a variety of chemical groups capable of combining with acids and bases. The state of combination of these groups is intimately related to the ability of wool to absorb moisture and dyes, its elastic and tensile properties, and its behavior in carbonizing, scouring and milling. In order to form a background for investigations relating to these technologically significant properties of wool, an extensive investigation of the acidic and basic properties of the fibers has been undertaken. Information obtained from such an investigation should also aid considerably in the further elucidation of the chemical and physical structure of wool fibers.

The present study is concerned with the description of the relation between amounts of hydrochloric acid and potassium hydroxide bound by wool and the concentration of these substances in solution. The effect of the presence of added neutral salt, potassium chloride, on this relation has also been studied. Although the maximum amounts of acid or base bound are independent of the presence or absence of salt, the way in which this maximum is approached depends very greatly on the presence of salt, and varies with the amount. Thus, the range of concentrations of acid in which the amount of acid bound increases from zero to near its maximum value is relatively narrow when salt is absent. Since this is also true of combination with base there is a wide region in the middle of the acid-base scale in which no combination with either can be detected. In the presence of even small concentrations of salt, the course of combination is more gradual, and the point at which no combination with either acid or base occurs is sharply defined. The higher the concentration of salt present, the lower is the concentration of acid or base at which any given amount of either is combined. This dependence is so marked that, in dilute solutions, doubling or tripling the concentration of salt has practically the same effect as doubling or tripling the concentration of acid or base. It is shown that all these effects of salt are manifestations of the same restriction: the fiber must combine with or adsorb equivalent quantities of both positive and negative ions. Thus, its ability to combine with hydrogen ions is limited by the simultaneous availability of chloride ions. By interpreting the combination with these accessory ions in terms of the partial dissociation of protein salts formed by combination with acid or base, the details of the difference between the curves of combination in the absence of added salt and in the presence of different concentrations of added salt are fully explained. This interpretation also leads to the prediction that the data of acid combination obtained in the presence of high concentrations of salt should correspond very closely with the results that would be obtained if wool could be studied in the dissolved state. By comparing the data obtained for wool with data for a soluble protein, egg albumin, which contains the same proportion of different acidic groups, this prediction is verified. On the basis of this comparison and by analogy with similar work on other soluble proteins, the curves relating the amount of acid combined to degree of acidity are resolved into component parts which are consistent with previously published figures for the amino-acid composition of the fiber.

The demonstration that the combination of anions with the fiber is a limiting factor in the combination with acid may prove to be significant in the process of acid dyeing. In this process, competition between the colored dye anions and the simple anions of the commonly used Glauber's salt may play a part.

## PART I

### I. INTRODUCTION

THE nature of the dependence on pH of the degree of combination of acid and base by such insoluble proteins as wool, silk, and collagen, differs in certain characteristic ways from that of soluble proteins. Examination of measurements reported by Speakman and Hirst[43], Lloyd and Bidder[34], and others leads to the conclusion that the titration curves of these three proteins, determined in the absence of salt, are distinguished from those of all soluble proteins so far studied† under the same conditions in three principal respects:

*The state of combination of wool with acid and base is intimately related to its ability to absorb moisture and dyes, its elastic and tensile properties, and its behavior in carbonizing, scouring, and milling. In order to form a background for researches relating to these technologically significant properties of wool, an extensive investigation on the acidic and basic properties of the fibers has been undertaken.

Part of the material in the present paper was presented at the meeting of the American Society of Biological Chemists at Toronto, Canada, in April, 1939.

**Research Associates at the National Bureau of Standards representing the Textile Foundation.

†Except those, such as hemoglobin, in which irreversible effects occur[10, 27].

(1) They show a long region of little or no acid- or base-binding capacity, more or less symmetrically placed about the point of neutrality. This is true even when, as in the case of wool and silk, they contain appreciable quantities of histidine which, because of its imidazole group, should function as a buffer in this region.

(2) The amounts of acid and base bound increase sharply as the extremes of the pH scale are approached and reach their respective maximum values at about the same pH as in the case of soluble proteins. Thus, the titration curves are steeper than those of soluble proteins, or of soluble polybasic acids in general.

(3) The pH values at which half of the maximum amount of acid or base is combined (a convenient measure of the position of the curve and, in simple substances, directly related to the acid strengths of the groups titrated), are shifted considerably toward the two extremes of the pH scale. Thus, the S-shaped portions of the curves found on the acid side of pH 7 are centered, in the case of almost all dissolved proteins, about a pH very close to 4.0, but in earlier published work on wool this point appears to be 2.3[43, 44, 45]. If these curves are regarded as resulting from the titration of many groups which possess identical dissociation constants this difference in the position of the midpoints would represent a fifty-fold increase in the acid strength of the insoluble protein, although its dissociating groups are presumed to be the same as those present in proteins which may be titrated in the dissolved state.

This description of the striking differences between the titration curves of soluble and insoluble proteins is made more concrete by the comparison in Figure 1 of the data for wool (obtained as described in the experimental section) with similar data of Kekwick and Cannan[31] for the soluble protein, egg albumin, both at 25° C. The latter are chosen because of their general excellence, and

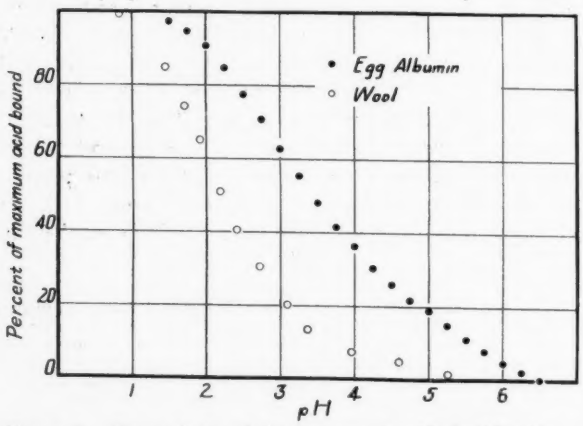


**Figure 1. Comparison of the curves of acid combination of wool and of egg albumin at 25°, in the absence of added salt.**

the close similarity in relative composition of egg albumin and wool, with respect to those amino acids (aspartic acid, glutamic acid and histidine) which should affect the shape and position of their titration curves* in the acid region, although these proteins differ considerably in their combining weights. The same scale of ordinates is used for the two curves by plotting, instead of the amount of acid combined per gram by each protein at each pH, the fractions of the total amounts of acid which are required to bring them from a condition of equilibrium with a solution at pH 6.4 to one at pH 1 (the reason for choosing pH 6.4 will be apparent later). These curves are typical of those obtained over this range of pH with proteins of the two classes, and illustrate: (1) the long region, starting below pH 5 (and extending to pH 10) in which practically no acid combines with wool; (2) the much greater steepness of the curve for wool; (3) the much greater acidity at which half the maximum amount of acid is combined.

Cannan has shown that this portion of the curve for *egg albumin* (after correction for the small amount of acid combinations due to histidine) is readily described in terms of the law of mass action, using only a single dissociation constant, if allowance is made, in a semi-empirical way, for the effect of electrostatic interaction between the ionized carboxyl groups on their respective dissociations[4]. Clearly, if a similar analysis is to be applied to the data for wool, additional factors must be taken into account. A possible clue to the nature of the difference is suggested by the fact that the steeper slope characterizing the curves for the insoluble proteins may be described to a good degree of approximation by substituting $(H^+)^2$ for $(H^+)$ in the mass law expression for egg albumin used by Cannan.

It seems likely that these differences, characteristic not only of wool but of other high-molecular insoluble proteins as well[34], are necessarily associated with the presence of a separate phase. Nevertheless, many proteins which are relatively insoluble at their isoelectric points have hitherto been titrated in the presence of much undissolved material over at least part of the total range of the titration. Singularities and discontinuities, which may not be an essential part of the titration phenomena but rather the result of the disappearance or appearance of a second phase, have appeared in these data[5].

Among those who have recognized the existence of these differences between the titration curves of dissolved and undissolved proteins, Speakman and his collaborators[43, 44, 45] and Lloyd and Bidder[34], have preferred to attribute them to fundamental differences between the structures of insoluble and soluble proteins rather than to factors introduced by the existence of two-phase equilibria. Thus Speakman appears to believe that salt linkages, between acidic and basic groups, prevent the functioning of these groups in their customary ranges of acidity because

*The position and form of the acid titration curves are determined by the carboxyl groups of the protein rather than by the amino groups, because the latter are present as internally ionized ammonium-like salts. Thus the process of acid combination consists in replacing a proton on an ionized carboxyl group. The maximum amount of acid combined is, of course, determined by the number of amino groups[2, 7, 24].

certain minimal acid or base concentrations must be exceeded before such salt linkages are broken. This is equivalent to postulating a large charge effect transmitted through the solvent medium, on the dissociations of these groups. In view of the high dielectric constant of water, the postulated magnitude of this effect is open to question[2]. In addition, Lloyd and Bidder, working with collagen, gelatin, silk, and horse-hair, attribute a part of the inactivity of acidic and basic groups at reactions near neutrality to the existence of vaguely-defined covalent linkages between adjacent polypeptide chains, which render the groups in question unavailable until these linkages are destroyed by exposure to sufficiently concentrated acid or alkali.

Nevertheless all of these authors, and others who have been concerned with the electrochemical and osmotic behavior of insoluble proteins, have recognized that account must be taken of the presence of two phases, and have had recourse to the usual method of describing such phase equilibria by means of the Donnan equations[12, 13], at least in a qualitative way. A *quantitative* analysis of the titration curve, sufficient to decide the extent to which the existence of two phases eliminates the need to consider other factors of the kind mentioned above, has not hitherto been made. The reason for this is not far to seek: there are grave difficulties in defining, without arbitrariness, the compositions of the phases in applying the equations of the Donnan equilibrium to the cases in question. In the present paper new data on the combination of wool with both acid and base are described in terms of a more readily defined and simpler concept. This treatment does not pretend to supplant the treatment of Donnan in other cases of two-phase equilibrium for which exact information as to the composition of clearly delimited phases makes possible its proper application.

As a result of certain theoretical considerations*, it appeared likely that data obtained in the presence of neutral salt at constant ionic strength might shed light on the cause of the differences apparent between curves obtained with acid alone (Fig. 1). The measurements to be described here, most of which were made at 0° C. to avoid complications introduced by hydrolytic decomposition, have led to a simple and general way of relating these differences to the conditions under which insoluble proteins such as fibers must be titrated. It seems probable that the resulting viewpoint has consequences for many phenomena characteristic of soluble as well as of insoluble proteins. Thus, for example, in the study of the effect of pH upon protein solubility a condition necessary for measuring the phenomenon is the presence of the solid phase.

## II. EXPERIMENTAL PROCEDURE

### 1. Material

Raw wool fibers were cut into root and tip portions, and the latter, which are contaminated and partially decomposed, were discarded. The root portion was purified by washing in cold ether, extracting for 16 hours, first with alcohol and then with ether, at temperatures below 35° C., and finally washing repeatedly in distilled water. It was carded by hand or on a sample carding machine†, rewashed in distilled water, air-dried, and finally conditioned at 21° C. and 65 per cent relative humidity before weighing. Analyses for total nitrogen, amide nitrogen, primary amino nitrogen, sulfur, and cystine gave nearly identical results with all the batches of wool used. Analyses for ash were made by combustion, and by an adaptation of the electrodialysis method of Joseph and Stadie[30, 48]. Most of the data on combination of acid at 0° were obtained with wool containing only 0.10 per cent ash. No effort was made to remove this ash and no correction was applied for its effect (shown to be very small, see III-1) on the amount of acid combined. The remaining data, obtained with material of higher ash content (0.26 per cent), were corrected for the alkali equivalence of the ash by subtracting from or adding to the measured acid- or base-binding capacity an amount determined by direct comparison with the low-ash wool, occasionally supplemented by other methods of estimation**. The moisture content of the fibers used in each experiment was determined by drying representative samples for two hours in a vacuum oven at 105° C. The data are expressed as acid or base bound per gram of dry wool.

### 2. Methods

(*a*) *Titration with Acid*—Samples of wool weighing either 1.2 or 2.0 g. and containing from 13.1 to 15.0 per cent of moisture, were placed in 100-ml. portions of acid solutions at the temperature of the experiment (0° or 25° C.). The solutions contained varying amounts of hydrochloric acid and sufficient potassium chloride to bring them, after absorption of acid by the fibers, to predetermined ionic strengths between 0.005 and 1.0. Sets of solutions containing only HCl, without added salt, were also used. Rapid and complete wetting-out of the wool was facilitated by pumping off air with a filter pump. Repeated preliminary sampling showed that during immersion over a period of 48 hours at the lower temperature, there was a perceptible drift of pH in solutions from which a large fraction of the total acid was removed by combining with the wool. Therefore, in order to assure attainment of equilibrium, the fibers were exposed to the solutions at either temperature for periods of from 48 to 75 hours before samples were withdrawn. Portions of each solution, transferred to stoppered Pyrex test-tubes, were allowed to come to room temperature (22° C.-31° C.) and the pH of each was determined. Aliquots of the original solution and of the solution in equilibrium with the wool were titrated with sodium hydroxide, using bromcresol purple as indicator. From the difference between these titers, the weight of the sample, and its content of moisture, the amount of acid taken up per gram of dry wool was

*These considerations are discussed in Section IV.

†Thanks are due to the Eavenson and Levering Company of Camden, N. J., for carding four batches of wool used in this work.

**The principal alternative method used was an electrodialytic estimation of combined base, by an adaptation of the method of Joseph and Stadie[30].

calculated. Since differences in titers are involved, and since these differences do not change in direct proportion to the total concentration of acid, the measurements made in the most acid solutions are most subject to error. This limitation of accuracy was partly offset by using the larger wool samples in the most acid solutions.

The chloride disappearing from solution was determined by titrating the same aliquots, after neutralization, with 0.1 *M* silver nitrate. Sufficient potassium chromate solution to bring the chromate concentration above .01 *M* was used as indicator. Errors caused by end-point uncertainties were reduced by matching the colors of the aliquots with one another.

In calculating the hydrogen ion and chloride ion bound by the fibers from the difference in titers of the solutions, proper account was taken of the effect of water absorption by the fibers on the final concentration of acid. With the ratios of fibers to solutions used, this correction was negligible except when the acid concentration exceeded 0.1 *M*, but the importance of this procedure has been amply demonstrated by critical experiments with ratios more favorable to the detection of effects due to moisture absorption. In calculating these small corrections, it has been assumed that the hydration of the fiber is the same in acid solutions as it is in water, and that no hydrochloric acid is dissolved in the water taken up. Recent unpublished measurements on cotton fibers in this laboratory indicate that the latter assumption may not be strictly true, but only a slight over-correction results from its use. Omission of the correction would result in an apparent decrease in the acid bound when the concentrations of acid exceeded 0.2 *M*.

In order to determine whether prolonged exposure to acid produced significant hydrolysis of amide bonds, other aliquots from each solution were tested for ammonia with the Nessler reagent of Koch and McMeekin[33]. At 0° C., only the highest acidities used (over 0.2 *M*) produced a detectable amount of ammonia (.06 mg. per g.). The effect of this amount on the titration curve is practically negligible. At 25° C., concentrations over 0.1 *M* produced sufficient ammonia to account for 0.01-0.03 millimole of acid combined. This is equivalent to hydrolyzing from 1 to 2 per cent of the amide groups present. Tests with the phenol reagent of Folin and Ciocalteu[14] showed the presence of traces of a reducing substance in the most strongly acid solutions. This appeared to be present in the wool before treatment with acid rather than to result from decomposition since the maximum amount found was the same at both temperatures. Negative sulfide and biuret tests on the solutions showed that no appreciable dissolution or decomposition nad occurred.

(*b*) *Titration with Base*—Portions of wool weighing either 3.0 or 4.0 g. were placed in carbonate-free alkaline solutions (usually in volumes of 200 ml.) at 0° C. The solutions contained varying amounts of potassium hydroxide and sufficient potassium chloride to bring the total ionic strengths to predetermined values of 0.02 or 0.2 *M*. Sets of solutions without added salt were also used. The larger samples were used in the most alkaline solutions. Although it is very desirable to limit the time of exposure to alkali to a minimum in order to minimize the amount of decomposition, control experiments at acidities at which decomposition was negligibly slow showed that periods of immersion of at least 18 hours were required to attain equilibrium. Approximately 20 hours was allowed in all the experiments reported, with the exception of those mentioned later.

In determining the amounts of base bound the procedure of Harris and Rutherford[25] was followed except for the substitution of bromcresol purple for methyl red as indicator, and the use of nesslerization for the determination of dissolved protein. Additional aliquots were used for immediate measurement of pH at the temperature of the experiment. The use of bromcresol purple reduced the error introduced on the acid side of pH 6 by the buffering capacity of dissolved protein in those solutions in which appreciable decomposition has occurred*.

A slight modification of the method of calculating the corrections was introduced. Comparisons of the ratio of dissolved nitrogen, after Kjeldahl digestion, to dissolved inorganic sulfur with the same ratio in the intact protein indicated that a small fraction (usually from one-tenth to one-fifth) of the inorganic sulfur in each solution was derived from the wool that had dissolved. Therefore, only the remaining eight- or nine-tenths of the inorganic sulfur in solution was produced by hydrolysis of disulfide bonds *in the undissolved wool*. Only the latter portion should be included in the correction for disulfide bonds broken since the base taken up by the dissolved protein, including that taken up by the sulfhydryl groups formed by hydrolysis of its own cystine, is not measured by the differential titration method used in this work.

This modified correction was shown to be justified by control measurements with several different concentrations of potassium hydroxide between 0.05 and 0.30 *M*, and with periods of immersion between 1.5 and 27 hours at 0° C. These measurements showed that with the highest concentrations there is a measurable increase in the amounts of base combined up to at least ten hours, and that after this period, the amount bound does not change if the constantly increasing corrections for decomposition are properly made. If on the other hand the corrections are applied as in the method of Harris and Rutherford, the calculated amount of base bound decreases somewhat on prolonged exposure to strongly alkaline solutions. This would be the expected result of over-correction when the amounts of decomposition become large. The same effect is evident when results at different concentrations of potassium hydroxide, obtained after the same times of exposure, are compared. The calculated amounts of base bound tend to *decrease* at the highest concentrations if the correction for *all* the inorganic sulfur is applied.

At 0° C. the largest correction, 0.28 milliequivalent per

*Buffering capacity on the alkaline side of the pH for zero combination is taken care of by the methods of correction for the effects of decomposition used by these authors.

gram, corresponded to the destruction of approximately one-half of the disulfide bonds and the dissolving of one-twelfth of the total protein. In similar controls carried out at 25° C. as much as 85 per cent of the cystine was destroyed, and up to one-sixth of the protein dissolved. With these larger amounts of decomposition, the necessity for modification of the method of Harris and Rutherford was even clearer. Thus, while the modification described here gave consistent results at the two temperatures, the unmodified corrections gave lower values at high concentrations of potassium hydroxide at the higher temperature.

Since the earlier measurements of Harris and Rutherford were obtained, for the most part, after exposure of wool to alkali for two hours, and since the corrections subtracted were slightly high, their values for the amounts of base bound are probably a little lower than the true equilibrium values. The data of the present investigation indicate that the maximum possible amount of base has not been bound even at potassium hydroxide concentrations of 0.3 *M*. However, the protein may be modified by decomposition of bonds other than disulfide when these or higher concentrations of alkali are used, and the methods of correction applied here may no longer suffice.

In view of the magnitude of the corrections described, no additional corrections for the effect of water absorption by the fibers on the calculated amount of combined base were applied. The small effect of this correction is within the error of the values given.

(*c*) *Measurement of pH*—Measurements of pH were made with the glass electrode assembly developed by MacInnes and Belcher[35], connected with a thermionic potentiometer which employed a cathode-ray "eye" as null indicator. The potentiometer, arranged to read directly in pH at temperatures between 0° and 30° C., could be set reproducibly to 0.002 pH unit when measuring buffered solutions. The following solutions[29] were employed in establishing the pH scale in terms of which the measurements at 25° are expressed: (a) 0.1 *M* hydrochloric acid, and (b) 0.01 *M* hydrochloric acid plus 0.09 *M* potassium chloride, using the values 1.085 and 2.078, (c) 0.05 *M* potassium hydrogen phthalate, using the value 4.008, (d) 0.1 *M* acetic acid plus 0.1 *M* sodium acetate, using the value 4.648, (e) 0.05 *M* sodium tetraborate, with the pH value 9.180. In addition, 0.05 *M* potassium hydroxide was used. A pH of 12.61 was assigned to this solution, consistent with the activity coefficient (0.824) determined by Harned and Cook[20] and the value of Harned and Hamer[22] for the ion product of water (pKw = 13.997).

Calibration at 0° C. was carried out with the same solutions, omitting the sodium tetraborate. The same pH values were assigned to the hydrochloric acid and phthalate[18] solutions at both temperatures, but the value assigned to the acetate buffer at 0° C. (4.673) was estimated by adding to the value at 25° C. the logarithm of the ratio of the dissociation constants at the two temperatures. The negligible effect of temperature on the activity coefficients of the ions in these solutions is thus not taken into account in the values assigned. The pH assigned to 0.05 *M* potassium hydroxide at 0° C. was 13.56, estimated from the value of Harned and Hamer at this temperature for pKw (14.94) and the activity coefficient (0.829) determined by Harned and Cook.

When the pH-meter was set at the proper pH with any of these standards except the most alkaline one, each of the other four buffers could be read to within 0.01 pH unit of the values assigned to them. Readings in alkaline solutions required adjustment for the departure, at pH greater than 9, of the slope of the pH-e.m.f. function from its theoretical value. This adjustment was carried out as follows: after setting the pH-meter to read 4.008 with the phthalate buffer in the electrode vessel, the pH reading of 0.05 *M* potassium hydroxide was determined, and subtracted from the calculated correct reading. The difference (never over 0.26 pH unit at 0° C.) was assumed to be uniformly cumulative over the pH interval of 8.55 units. This is equivalent to assuming that over this range of pH the proportionality between e.m.f. and pH is lower than the proper value of RT/F by about 3 per cent. This assumption leads to adjustments which are subject to most error at pH 7 to pH 10. In this interval only a few readings were taken; and owing to the relatively small slope of this part of the titration curve, a small error in pH has very little effect on its shape or position. The pH values reported for alkaline solutions are less certain than those in the acid range because of these adjustments (based in part on a *calculated* pH) and because of some hysteresis of the glass membrane after exposure to concentrated alkali. The latter sometimes introduced a discrepancy of .03 to .04 pH unit, apparent when the measurements of acid standards were repeated after an alkaline series. In agreement with the work of Dole and Wiener[11] the required adjustments and the residual uncertainties are larger at the higher temperatures.

The pH values of alkaline solutions were measured with the electrode assembly mounted in an air thermostat at either 3° C. or 25° C. Solutions were introduced and manipulations made from the outside. The results given at 0° C. are calculated from measurements made at the lower temperature. Practically all acid solutions were measured at room temperature. Since many of the solutions were very poorly buffered, the accuracy of a large number of the measured pH values was tested by direct comparison with the calculated values based on the titer of the solutions and the activity coefficients of the acid or base[19, 20, 21, 22, 26]. With solutions more acid than pH 3.5 at ionic strengths below 0.1 *M*, agreement to .01 pH unit was usually found. The presence of *traces* of a soluble buffering substance derived from the wool reduced this agreement in the range pH 4 to 10, but in the absence of wool this agreement extended to pH 4.5, beyond which the concentration of HCl could not be accurately determined. The stability and reproducibility of the measurements below pH 6 render it very probable that the same

***(Continued on page 121)***

# • TECHNICAL NOTES FROM FOREIGN SOURCES •

## The Prevention of Dull Shades Due to the Presence of Iron in the Dyebath, When Dyeing with Chrome Dyes. Part 1—Iron in the Water Supply

*C. L. Bird and E. Molloy—Jour. Soc. Dyers and Col.*, 55-11, *November*, 1939.—The dulling effect on dyed shades caused by dissolved iron in the dyebath has been recognized as more pronounced in the case of dyes applied in an acid bath, such as acid and chrome dyes, than in the case of those applied from an alkaline bath, such as vat and sulfur dyes. Chrome dyes, as a class, are more readily affected by iron than are the acid dyes, though they are less susceptible when dyed by the metachrome process or on a chrome mordant. Very small amounts of iron give rise to dull shades with certain chrome dyes which are especially sensitive. With such a dye 0.4 part of iron per million parts of water is sufficient to dull the shade, while one part per million will completely alter it.

Three products have been recently recommended for preventing the dulling effect of iron in the dyebath. These are: (1) Calgon T, a mixture of approximately 80 per cent of sodium hexametaphosphate and 20 per cent sodium tripolyphosphate; (2) acid sodium pyrophosphate and (3) Trilon B (I.G.), which is probably the sodium salt of trimethylamine-a:a′:a″-tricarboxylic acid, together with some sodium carbonate. Employing these compounds and also two other phosphates, tetrasodium pyrophosphate and sodium tripolyphosphate, experiments were carried out to determine the protective effect of such agents in dyeings made with dyes selected as particularly sensitive to iron, in baths of a known iron content.

The two commercial dyes selected for the test were Eriochrome Verdone S (Colour Index No. 292) and Solochrome Dark Blue BS (Colour Index No. 202). One per cent dyeings were made on unbleached scoured woolen cloth, adding varying amounts of protective agents and dyeing assistants. The colors of dyeings thus obtained were recorded in units of red, blue and yellow by means of a Lovibond Tintometer.

Observations are recorded in several tables, and three graphs are employed to illustrated results obtained. It is concluded that Calgon T, acid sodium pyrophosphate, Trilon B, tetrasodium pyrophosphate and sodium tripolyphosphate all possess in varying degrees the property of sequestering small amounts of dissolved iron in the dyebath, sufficient to prevent the formation of iron lakes when dyeing with chrome dyes. It is also confirmed that, in the metachrome and chrome in the bath processes, the presence of potassium bichromate or chromate throughout the dyeing process affords good protection against iron. The protection is less effective when dyeing on a chrome mordant.

## Application of Vat Dyes to Viscose Rayon

*J. Boulton & T. H. Morton—Jour. Soc. Dyers & Col.*, 55-10, *Oct.*, 1939.—A detailed study, with emphasis on the practical significance, of dye bath phenomena observed when dyeing viscose rayon with a large number of vat dyes. The communication is from the Textile Research Laboratories of Courtaulds, Ltd.

Recent researches have shown that, in the case of direct dyes, ease of levelling on variable viscose rayon and of penetration into the fiber are determined by the rate of absorption of dye. The fundamental process involved in direct dyeing approximates to a process of diffusion. Under normal conditions, dye absorption has the kinetic characteristics of a diffusion process in which an equilibrium is reached between fiber and dyebath in a time which is specific for each dye for fixed conditions of temperature and concentration. There are *a priori* reasons for assuming that the mechanism of absorption of vat dyes by viscose rayon is fundamentally the same process.

In the case of direct dyes, exhaustion and diffusion rates run parallel, so that the more rapidly exhausting dyes are consequently found to be the more readily penetrating. As a class, the vat dyes are in general *rapid dyeing* as compared to direct dyes. They are, however, *poorly penetrating*, and the rate of exhaustion of the dye bath is not necessarily related to the rate of penetration.

Part II of the paper deals with the kinetics of vat dyeing. A method was developed for estimating vat dyes by use of the Colorimeter, producing stable colloidal suspensions of the oxidized coloring matter by treating the baths with hydrogen peroxide in presence of egg albumen. By this method the absorption of 7 representative vat dyes (four "strong alkali" and three "weak alkali" types) was studied, and a series of absorption-time curves for these dyes constructed. The dyeing behavior of a vat dye may be characterized by a complete absorption-time curve, and as the curves so obtained were similar in type to those obtained for absorption of direct dyes by viscose rayon yarn, it was concluded that the leuco-dye absorption is also controlled by a diffusion process.

To confirm this conclusion, observations were made on the diffusion of leuco-dyes in sheet cellulose, using a method which yields a relative diffusion constant for each dye. Sections of cellophane, clamped between steel plates so that only the cut edge was exposed, were treated with leuco-solutions at a fixed temperature (60°) for varying periods of time. Observations so obtained from four difrecent vat dyes are expressed in tabular form, in which measured distance of diffusion (D) and the time of treatment in minutes (t) are combined to express a series of constants, $D^2/t$.

***(Concluded on page 127)***

PROCEEDINGS OF THE
# American Association of Textile Chemists and Colorists

March 4, 1940

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## • CALENDAR • OF COMING EVENTS

Meeting, Philadelphia Section, Penn A. C., March 8, 1940. Speaker: Dr. R. E. Rose, du Pont Co., "1914-1939—A Contrast in National Independence."

Meeting, New York Section, Chemists' Club, New York, N. Y., March 29, 1940.

Meetings, Council and Research Committee, National Bureau of Standards, Washington, D. C., April 19, 1940.

Spring Meeting, Piedmont Section, King Cotton Hotel, Greensboro, N. C., April 27, 1940.

Annual Meeting and Convention, auspices New York Section, October 18th and 19th, 1940, Hotel Commodore, New York City.

# Three-Phase Light Sources

## of Interest to the Textile Industry as Applied to Accelerated Light Fastness Testing Equipment and Color Matching Lamps*

DR. M. J. DORCAS**

THIS paper discusses two subjects which at first glance may seem to have but little connection, but upon investigation it will be found that they have both a common factor that is of greater importance than any other single one, that is, a light source. These pieces of equipment are: machines for the accelerated testing of the fastness to light of dyed fabrics and other colored objects, and an artificial light to supplement or replace inadequate or varying daylight for the purpose of matching colors or determining the color of objects as practiced in the commercial classification of commodities. A typical example of this work is the classification of cotton.

We are all familiar with the process of testing colored objects to determine their fastness to light and the desirability of making these tests. Hence the development of a considerable number of machines for testing or predetermining this color stability in actual service. These machines usually consist of apparatus for exposing small samples to some form of light source that can be operated continuously so that the action of the light on the color can proceed day and night. The light is frequently made as intense as possible to hasten or accelerate the action and give information as soon as possible, hence the name accelerated testing equipment for this general type of apparatus.

Let us briefly study what happens when a dyed textile is exposed to light. When light falls on a colored object at least three things may happen. The light may be transmitted, it may be reflected, or it may be absorbed. Transmitted light is of but little interest to us in this discussion. Reflected light is of prime importance since it is reflected light that gives the color to the object. A white object, of course, reflects equal amounts of all kinds of incident light, a black object reflects practically none. A colored object selectively absorbs certain colors and does not absorb others, thereby giving a colored, reflected or transmitted radiation. The absorbed light, while not so obvious as reflected light, is of importance to us because in some cases absorbed light has the ability to cause chemical reactions. These reactions may result in a change of the dye so that a different amount or quality of light is reflected, thereby changing the color. When this occurs the dye is said to fade or become off-color and its usefulness as a dye is thereby diminished or eliminated. It is, of course, well known that many agents can cause alterations of color, such as, soaps, alkalies, laundry operations, etc., but at present we are concerned only with those caused by exposure to light.

Chemical reactions caused by light or radiant energy are in general known as photochemical reactions. One of the earliest known laws dealing with photochemical reaction is known as the Grotthuss-Draper Law, which states that only that light which is absorbed can cause photochemical reaction. In our study of the mechanism of fading dyes, then, we become interested in this light which is absorbed. Further study indicates that this is controlled by two factors, the spectral absorption of the material itself and the quality of the incident light. Since the spectral absorption of the material is another form of expression for describing color which is fixed for the particular case we are to test, we must turn our attention to the quality of the incident light.

In practically all cases the light which causes fading is sunshine or some simple derivative of it, that is skyshine or sunshine that has been filtered through a window glass such as is found in the interior of buildings. In general, it is found that dyes fade more rapidly when exposed to outdoor daylight than when exposed to daylight that has been filtered through a window glass. This is partially a result of intensity, light intensities out-of-doors being generally greater than those in the interior of buildings, but it is also sometimes explained as being due to a difference in the quality of the light. Outdoor sunshine contains more ultraviolet than that which is found in the interior of buildings, as ordinary window glass absorbs or filters out part of the ultraviolet of sunshine. From this fact it is sometimes stated that ultraviolet is the part of the sun's radiation which causes fading and from this statement is deduced the idea that an ultraviolet source is the proper source to use in an accelerated testing machine.

This is not necessarily a correct conclusion for the following reasons: Different kinds of light, that is, different colors or different spectral qualities of light are capable of causing different kinds of reactions. A simple but typical illustration of this is the effect of different colored visible light on the old-fashioned photographic film. The old film was sensitive to blue light and not at

*Presented at meeting, New York Section, October 27, 1939.
**National Carbon Co.

all affected by red light. Very small quantities of blue light or ultraviolet profoundly affected the film but it was so little affected by red light that the ordinary developing processes could be carried out in the presence of considerable amounts of red light. This illustration has a definite bearing on the selection of a light source for use in an accelerated dye fading testing apparatus.

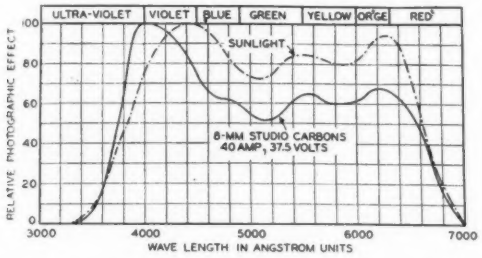



**Fig. 1—Photographic effect from studio carbon arc compared with that from sunlight showing the close similarity of natural sunlight and the Sunshine carbon arc throughout the spectrum.**

Since a very large number of colored substances are used as dyes and each has a different ability to absorb light and since in general each different color or wavelength of light has a different ability to cause a chemical change, it follows that different kinds of light sources may give different kinds of chemical effects or, in practical terms, a different color change when applied to the dye.

The practical object of accelerated dye fading equipment is to determine the probable serviceability or light fastness of the colored object when exposed to sunlight or some of its derivatives. Therefore, it is necessary if we are to get a true prediction of this serviceability in light, that we use a light that is qualitatively like sunshine because if we use a light that is different than sunshine in its qualitative nature, we may get a different kind of chemical reaction or a different fading effect than will be experienced when the material is exposed to natural sunshine. There are, no doubt, many cases where only one kind of photochemical change can or does occur. In these cases it would make no difference what form of light we used for our test equipment. Unfortunately, we do not know which particular colors will respond in this manner. Since we know that some dyes can act in different ways, depending upon the kind of light source to which they are exposed, it is necessary if we are to have an apparatus that will give us reliable predictions, that we get a light source as nearly as possible like the sunshine which will be our destructive agent when the material goes into actual service. It is practicable to determine the character of sunlight with considerable certainty. Modern physical instruments and methods have been applied to the study of sunlight and we now know its nature with considerable precision. Sunlight in general can be described by stating in physical terms its quantity or intensity and its quality or spectral energy distribution. Spectroscopic and radiometric equipment that analyze the beam of sunlight by dispersing it into its colors and measuring the intensity of each color or wave length are available in many laboratories. Sunlight as investigated by these instruments shows that it consists of a practically continuous spectrum running from about 2900 Angstroms on the short wave or ultraviolet side up to about 40,000 Angstroms in the infra-red.

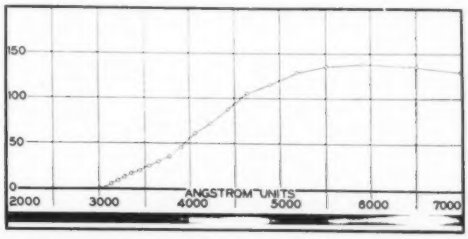



**Fig. 2—Spectrogram and energy radiation curve of natural sunlight.**

Figure 2 illustrates this in graphic terms. The quantity or intensity of sunlight is an exceedingly variable thing. It varies from perhaps 50 foot candles in the middle of the day in a smoky community in the winter time to a maxmium of 15,000 or 16,000 foot candles of visible light in a clear location in the middle of the summer. From these extremes in each day it starts from a minimum of nothing from dawn to dark to this variable maximum during the day. No two specimens or samples of sunshine agree precisely in quantity and likewise there is some difference in quality. In early morning and late at night the sunlight has a rather reddish tinge, the proportion of red diminishing during the day toward noon and increasing again at night.

To this direct sunshine daylight has added to it some skyshine which is a considerably bluer light, but still of the same diffused type of spectrum and of approximately the same extreme limits of wave lengths.

If we accept the hypothesis that the light source used in an accelerated testing machine should be a duplicate, if possible, of sunshine and if we have the known characteristics of sunshine, the problem now becomes an examination of existing light sources to determine which of them, if any, are suitable for this use. Analysis of radiation from different light sources has given us data about many types of radiation that are practically and commercially available.

Figures 5, 6, 7 and 8 show detailed spectral energy distribution curves of these various light sources.

From an investigation of a very large number of graphs and analyses of various types of radiation we have come to the conclusion that the Sunshine type of carbon arc is the most nearly like sunshine of all the commercially available light sources. It has an approximately continuous spectrum and the relative proportions of different types of wave lengths are as much like sunshine as any particular sunshine is like another kind of sunshine. These sim-

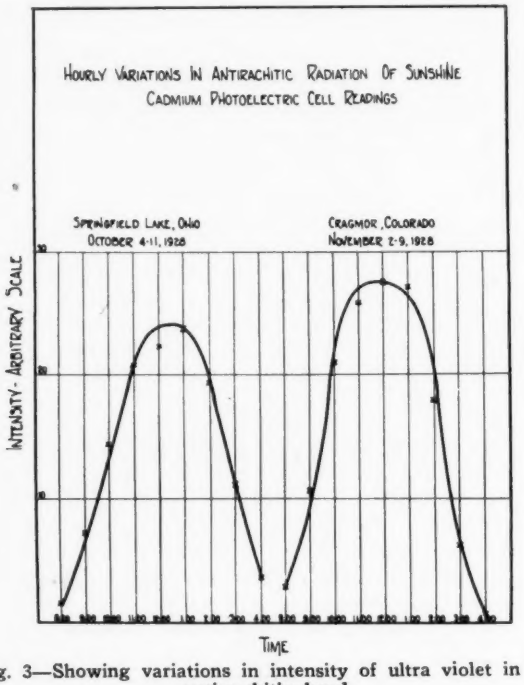



Fig. 3—Showing variations in intensity of ultra violet in the anti-rachitic band.

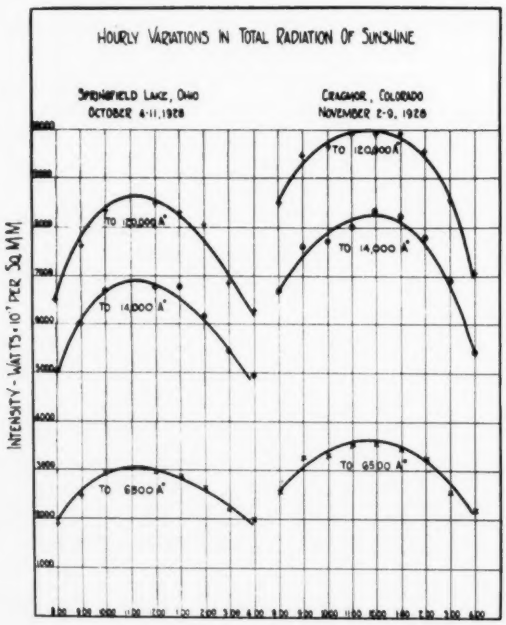



Fig. 4—Lower curves show variation of ultra violet and visible spectrum; center curves include penetrating red and infra-red; top curve includes non-penetrating infra-red.

ilarities between this type of radiation and sunshine are greater than between any other pair of illuminants, one of them being sunshine. A small proportion of the radiation from these arcs consists of an ultra-violet of shorter wave lengths than found in sunshine. This can

Fig. 5—A photograph of the Sunshine carbon arc.

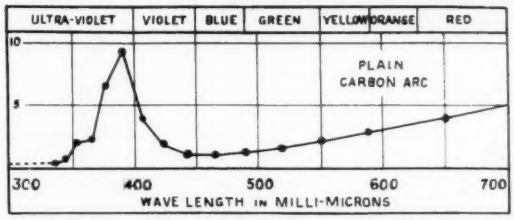



Fig. 6—Special energy distribution curves of plain (uncored) carbon arc.

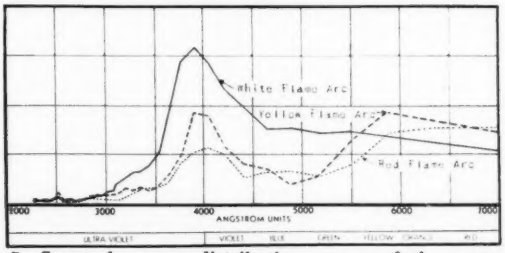



Fig. 7—Spectral energy distribution curves of three types of carbon arcs. The Sunshine Carbon (white flame arc) with its relatively continuous distribution of the colors of the visible spectrum emits light similar to natural sunshine.

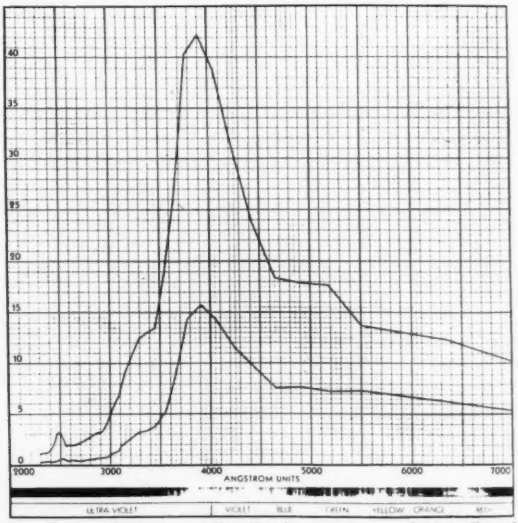


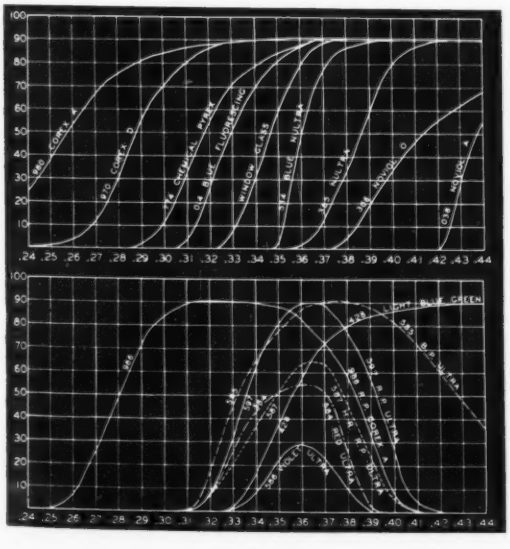

Fig. 8—Spectral energy distribution curves of the Sunshine carbon arc burning at 60 amperes A.C. (upper curve) and 30 amperes A.C. (lower curve—same as figure 7).

easily be corrected by interposing between the source and the point at which the radiation is to be used, a glass screen or filter which absorbs this type of radiation not found in natural sunlight. Several glasses of this type are available. A practical and easily obtainable one is Corex D, which has a transmission as shown in Figure 9, and the light of the arc through this is shown in Figures 10 and 11. Qualitatively this meets our requirements.

Intensity of carbon arcs can be varied enormously from very small ones to very large ones producing millions of candle power. The selection of the proper electrical characteristics of the lamp circuit enables us to get any required quantity or intensity of radiation.

This conclusion that the sunshine type arc is most suitable for the work is not an original one. In a paper published in 1915 Mr. William Mott came to the same conclusion after testing several hundred samples of dyes then in use with respect to their resistance to fading in sunlight and in the presence of various types of artificial illuminants. He did not at that time have the advantage of some of the modern spectrometric equipment and outside of the visible part of the spectrum his knowledge of the similarity of the sunshine type arc and the natural sunshine was based on the similarity of the results obtained. The subject of accelerated testing of dyed fabrics was not new at that time, since in his paper he has accumulated a bibliography of sixty-nine references bearing more or less on the subject. In spite of the fact that it was an old subject at that time, I have not been able to secure a picture of the equipment used prior to this time. I have a picture of Mott's apparatus. It is a picture of the first or oldest practical equipment for the accelerated testing of dyed fabrics that I have been able to find. Figure 12 shows this apparatus.

**Fig. 9—Light transmission of various glasses. Ordinates are percentages of transmission and abscissa readings are wave lengths in microns.**



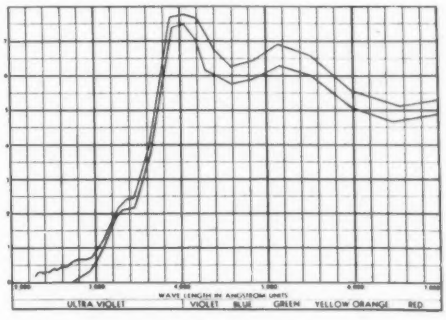




**Fig. 10—Spectral Energy distribution curve of "National" High Intensity Sunshine Carbons. Upper curve with bare arc. Lower curve with Corex D glass cutting out wave lengths below 2800 Angstrom Units which do not appear in sunlight.**

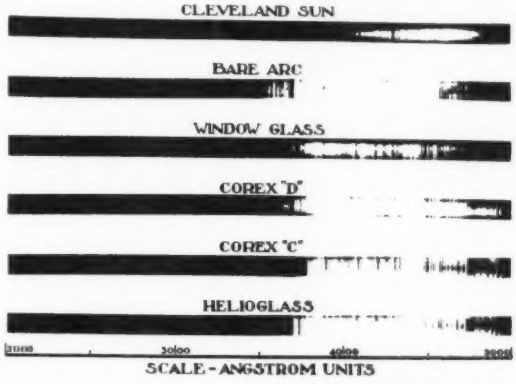



**Fig. 11—Spectrum of "National" Sunshine arc through various glasses.**

It will, as you see, consist of very simple parts. It was an arc lamp, a street lamp, as used in those days, suspended in a barrel. Samples to be exposed were placed around the interior of the barrel. This apparatus was an improvisation from materials easily available and according

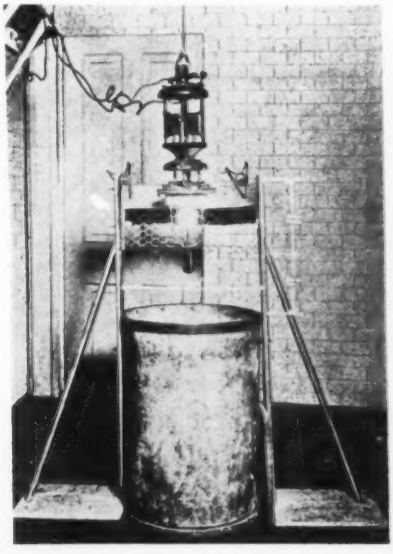


**Fig. 12 — Earliest practical equipment for accelerated testing of dyed fabrics.**

to modern standards seems quite crude. On careful investigation, however, it will be seen to have all the essential constituents of the modern types of machines. It had a light source and around the light source a support for keeping the samples in place. Modern instruments are more refined in their execution but still are essentially the same, that is, imitations of the lantern hung in a barrel. Even this crude equipment had specific advantages over testing with natural sunlight. It was constantly available day and night, summer and winter; the results were reproducible and, on using a Sunshine carbon in the arc, the apparatus was capable of giving an accurate prediction of the probable serviceability of the dyed fabric in actual outdoor exposure.

While the fading of dyes is a photochemical reaction, this photochemical reaction can be modified by a number of factors. The principal one is the presence or absence of water vapor. The stability of a dye toward light seems to be markedly affected by the presence or absence of water in the vapor form. One explanation of this action is that dyes are altered in light through a form of oxidation. Sometimes this is a direct oxidation and sometimes the presence of water vapor in the light is effective through the possible formation of hydrogen peroxide from the water vapor in the presence of the light, which in turn acts on the dye. There is, of course, a possibility of direct photochemical change on the dye molecule itself being catalyzed by the energy of the absorbed light without any dependence on reaction of oxygen or hydrogen peroxide. Most accelerated testing equipment provides some method of increasing the humidity, thus recognizing this effect of water on the photochemical change of the colored substance. In the past twenty-five years a number of commercial types of apparatus have been manufactured and sold and widely used. One is on display here tonight, together with some samples of colored fabrics that have been exposed in this machine with samples of the original and similar samples that have been exposed to outdoor sunlight for the purpose of comparison.

The machine exhibited consists of a three-phase arc between three carbon electrodes of the sunshine type, giving a light uniformly distributed in space around the arc, together with a row of sample holders arranged in a circle for exposing samples of fabrics to the radiation. Between the arc and the samples are interspersed sheets of Corex glass. The combination of sunshine carbon arcs and Corex glass, giving a light that is physically very similar to sunshine in its chemical or fading effect, is like sunshine or skyshine. The samples are suspended in a more or less closed container over warm water which exposes them in a humid atmosphere.

The arc consumes about a kilowatt of power, which gives an intensity of about 5,000 foot candles on the surface of the panels. This is equivalent to average daytime summer sunshine. It would be quite possible to use more power in the arc and give a higher intensity of light on the panels, thereby providing a more rapid fading action. The upper limit is controlled by the temperature which is permissible on the surface of the panels. Temperature of the samples, of course, varies with the color of the samples together with the texture. Dark-colored heavy fabrics may reach a temperature of 160° F., lighter-colored materials substantially less. A practical test is to expose samples of textiles, white or undyed, to make sure that they can stay there throughout the average life of the test without any discoloration not obtained when these same samples are exposed to actual sunshine. Samples of similar color and texture, when exposed to mid-summer mid-day sunshine acquire similar temperatures. By means of this maximum intensity of light similar to mid-day mid-summer sunshine, the high humidity obtained by maintaining the sample directly over warm water, and the fidelity of reproduction of sunlight obtained through the use of the sunshine type cored carbons producing a flame type arc and the Corex D filter eliminating any kinds of radiation not present in sunshine, it is believed that an instrument has been achieved that gives reproducible tests of color stability of dyed fabrics with a maximum reliability at a speed hitherto unattained.

A little while ago we spoke of light for color matching and commodity classification. Much of the theory of the selection of a light source for this type of application is simple, however complicated it may be in practice. The universal light source is sunshine plus skyshine. Most dyed textiles and commodities are viewed or inspected and largely used in daylight or some simple modification of it. Preparation of matched samples for inspection of colored objects that ought to be used or checked in daylight can be inspected under artificial light, if a few simple precautions are observed; simply that the light be com-

**Fig. 13—Modern, scientific dye fading apparatus producing fast and reliable results.**

parable in intensity and quality with the sunshine in which the objects will be used. The artificial light has a further advantage of being constantly available in uniform quality and intensity, releasing the inspector from the necessity of adapting himself to the vagaries of the weather. Modern technology has provided us with many lamps and light sources for a variety of purposes. Many of these are ingenious in their design and highly useful for display or spectacular purposes. They may be practically perfect for their purpose when used as a display and of no utility whatever with respect to providing a suitable light for color matching or color grading purposes.

An extreme but practical example is provided by the gaseous tube lights so frequently used for display purposes. For their intended purpose these lights are approximately perfect and are one of the marvels of our modern technical age. You have noticed, though, that objects have a somewhat unnatural appearance if inspected closely when illuminated by these fine lights. Particularly is this true of colored objects. They do not have the appearance that they have under so-called normal conditions, that is, light similar to skyshine plus sunshine or normal daylight. The reason for this abnormal appearance is simply that the light consists of one or a very few colors or wave lengths in the visible region and materials that are colored can reflect only light that is incident on their surfaces. Materials that might be very different in daylight may look practically alike during inspection under one of these lamps that give but limited spectra.

Extension of this philosophy leads us to the conclusion that the best possible light for color matching or inspecting things that are to be viewed in daylight is an artificial light that would be like sunshine. We have already established the fact that the sunshine carbon arc is essentially a duplication of sunshine or daylight and that for most purposes it can be considered a synthetic daylight. These arcs have been applied in a practical manner in the construction of artificial daylight or daylight equivalent lamps for color matching and commodity grading purposes. One is on display.

We assume from the above discussion the correctness of the selection of the quality of the light emitted from these arcs. We still have two questions to dispose of, namely: the intensity and its continuity with respect to time. As above stated, natural light constantly varies in quantity or intensity between exceedingly wide limits. Color matching and commodity grading is usually conducted under north skylights of substantial size. The intensities are somewhat variable, usually around from 100-350 foot candles on the work being done. Sometimes artificial light sources provide lower intensities than this, a practical upper limit being reached when the heat from the light source becomes objectionable to the operator. Because of the high efficiency of the carbon arc, that is, from 50-80 lumens per watt, depending upon the electrical characteristics of the arc itself, high intensities without objectionable heat are easily obtained. These intensities may reach 500 foot candles without the heat becoming noticeable. Most operations require considerable light intensity, especially when high speed of vision is required, but usually 150-300 foot candles will suffice for even the fastest operations. Such an intensity over an area of 25 sq. ft. or more is easily obtained with a lamp using about a kilowatt of power, the heat from which is negligible. The lamp on display tonight uses approximately one kilowatt.

In the practical application of arc lamps or other light sources several other factors must be considered. Glare is a prominent one. By placing the arc and its mechanism some distance above the operator and having sufficient area of the diffusing source which acts as a secondary light source, glare can be eliminated. The artificial light source simply replaces the illuminated skylight used when natural light is available.

Light is a complex thing and cannot always be entirely described by discussing the quality and quantity of the light. A typical illustration is afforded by the gaseous discharge or arc type of light, of which the carbon arc is one. Most power sources at the present time provide alternating current. Any form of light source that depends upon a gas for the luminous source, when excited by alternating current, is intermittent in character. On the ordinary 60 cycle current, alternating current, so universally available, this intermittency which amounts to 120 periods each second in which the light is alternately burning and extinguished is not noticeable under many conditions. If an object is at rest and viewed in this light, the persistence of vision in the human eye is such that we are not aware of these alternations in light, but when objects that are rapidly moving, such as the operator's hands, or samples, are inspected in this light, a flutter or jumping appearance is noticed which is called the stroboscopic effect. This is demonstrated by this small arc lamp operating on single phase, alternating currrent.

(Here demonstrated stroboscopic effect with the M-4 lamp.)

By the use of three electrodes, operating on three-phase electric current, the three phases being 120 electrical degrees apart, these periods of light and darkness overlap each other so that light is continuously emitted from the light source. This is diagrammatically illustrated in Figures 14 and 15. These three-phase arc lamps are not entirely new, they having been known theoretically for a generation or more. It is only in the very recent past that they have been developed in a practical form so that the advantages of color quality or spectral energy distribution of the sunshine arc could be utilized on the commonly available alternating current for color matching purposes as demonstrated with the lamp on display tonight. You will notice that the intensity is equivalent to full illumination under a large north skylight, there is no

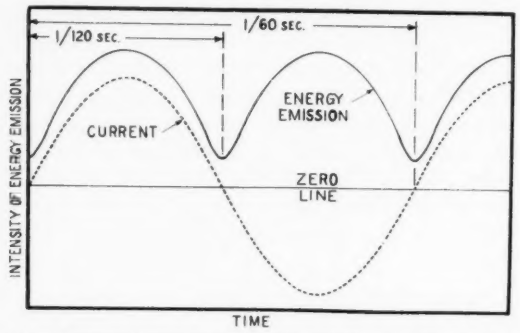



**Fig. 14—Current input and energy emission of 60 cycle single phase alternating current carbon arc lamp.**

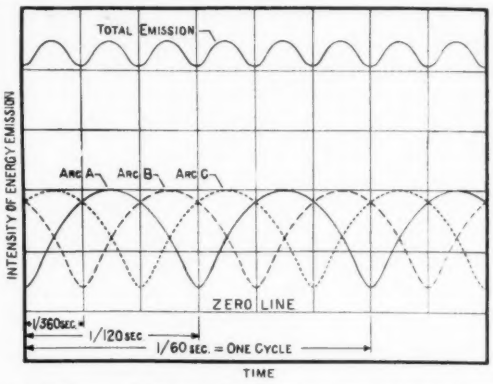



**Fig. 15—Energy emission of 60 cycle three phase alternating current crabon arc lamp.**

stroboscopic effect, objectionable heat is absent, and the color quality of the light is such that articles can be inspected under it interchangeably with natural light. I believe it to be an instrument of general utility to those concerned with critical investigations of the color of objects.

# Vinyon—A New Textile Fiber*

**DR. F. BONNET****

THE idea of obtaining textile fibers from gums and resins is, of course, not new. Dr. Robert Hooke mentions the matter in his Micrographia published in 1664 and later the French naturalist, Rene Reamur, refers to resin fibers in his book on insects published 1734 in these words:

"Silk is only a liquid gum which has been dried; could we not make silk ourselves with gums and resins?" In spite of these early suggestions the first silken fibers produced commercially were, of course, not made from gums or resins but from cellulose for the ordinary natural gums or resins are quite unsuited to be drawn or spun into useful textile fibers. It was not until the discovery of synthetic resins that this became possible.

With the discovery of the phenol-formaldehyde condensate resin Bakelite, followed by a host of other synthetic resins which go to make up the plastics industry today, many new properties of these resins became known; and while many uses have been found for these new plastic materials, only a very few have been found suitable for spinning into useful textile fibers.

Apparently only those thermoplastic polymers are suitable which are straight chain or linear polymers and the longer the straight chain is (i.e., the greater the molecular weight of the polymer) the stronger and more resilient will be the resulting fiber. All of which is best exemplified by the new polyamide resin nylon and the polyvinyl resin Vinyon, and like nylon it too can be said to be made of coke, water and air or better still from coke-lime-water and salt; but between these very basic raw materials there are, of course, many intricate steps before the textile yarn emerges.

"Vinyon" is a copolymer of vinyl chloride and vinyl acetate produced by polymerization rather than by condensation, as is the case with the phenolic, urea and alkyd and similar types of resins. Polymerization of the monomer may be brought about by irradiation with ultra-violet light; the addition of a small amount of peroxide or of ozone, and various catalysts. The polymers so obtained are straight chain or linear in which the monomers have reacted with each other at the double bond to form the high molecular weight polymers.

The vinyl chloride by itself gives a remarkably strong and tough film, but its softening, molding or flux temperature is so high that it is quite difficult to mill and mold free from strain. Hence plasticizers must be used if the right tensile and impact strengths and other good physical properties are to be retained. By the proper choice of plasticizers and thoroughly blending on a hot roll mill, a rubber-like material is obtained which can be molded or pressed into any desired shape. By varying the amount

*Presented at meeting, New York Section, January 26, 1940.
**American Viscose Corp.

of plasticizer or by adding fillers, pigments, dyes, etc., during milling, the properties of the resins can, of course, be modified. Because of the resistance of the resin to acid, alkali, salt solutions, fats, oils, etc., it has found use as sheets, rods, tubes, etc. Hence it seems to be replacing rubber for transmission belts not only because it has greater chemical inertness but because of its greater strength, its greater flexing life and its greater resistance to sunlight and all oxidizing and weathering effects.

The second polymer, namely vinyl acetate has properties quite different from the chloride. It begins to soften for example, only a few degrees above room temperature and its mechanical strength is not anything like that of the chloride. It cannot, therefore, of itself be used as a molding resin, but curiously enough it easily wets or clings to surfaces, acting as an excellent bonding material. In fact it is used as a binder in composition wood molding; as an adhesive for sealing fiber cartons; for making milk bottle caps; gumming tapes, etc. For especially sticky coatings plasticizers are used.

These acetate polymers burn very slowly with a smoky flame. They are colorless, tasteless, odorless, non-toxic but quite thermo-plastic. They are not affected by water, aliphatic hydrocarbons, the higher alcohols, etc., and have an excellent resistance both to light and heat maintaining their clarity even after long exposure to either.

Considering the remarkable properties of these two resins it might be thought that by carefully blending a series of resins would result in combining the attractive features of both, but unfortunately such is not the case. Even under the best of intimate mixing only weak, brittle or indifferent products result. When, however, the vinyl chloride and vinyl acetate are simultaneously polymerized, chloro-acetate resins result whose composition depends upon the predetermined proportions in which the ingredients are mixed. In fact the reaction proceeds in such a way that the vinyl acetate can be said to internally plasticize the vinyl chloride and the degree of plasticization can be controlled by varying the ratio of the two before polymerization. This type of plasticization is, of course, quite different from the usual type in which external plasticizers are used which are usually high boiling liquids, waxes, gums, etc. In many cases such external plasticizers are still essential but the resins so plasticized are always subject to a change in composition due to a loss of the plasticizer by evaporation, oxidation or solvent extraction.

In the case of internal plasticization where the polymers are actually combined, such changes cannot, of course, take place and the resins are stable.

While these copolymers have properties of both the chloride and acetate they do not represent merely an average of the properties of the individual polymers of which they were formed, for the resin molecule consists of a linear chain in which the two monovinyl compounds have reacted with themselves and with each other, the reactions taking place, of course, at the double bond and the relative proportions of the chloride and acetate in the chain will depend upon the reaction mixture, while the length of the molecule is governed by the reaction conditions at the instant of formation.

Of the various copolymers investigated only those containing 85 per cent or more of vinyl chloride seem to have particular industrial interest, although there is one containing from 65-70 per cent vinyl chloride which is of interest in the coating field. This has an average molecular weight of only 4000 to 6000 and because of its high acetate content is compatible with nitro cellulose. The resulting mixture provides a coating which is superior to either product by itself. Other coating polymers contain 85-86 per cent of the chloride, but of greater interest is the next higher series with 86-87 per cent chloride and molecular weights ranging from 8500-9500. The polymer in this case is large enough to give excellent toughness to the film while yet small enough to permit good solubility.

The next resin is one having a molecular weight of 9500-10,500 and was developed as a coating for paper and a similar one is used for phonograph records and floor tile. (Readers' Digest Records for the blind are being made on such records.)

For compression molding, resins with 85-88 per cent vinyl chloride are used having an average molecular weight of 12,000-13,000 while for the manufacture of plastic sheets where outstanding strength and toughness are required a resin with 88-90 per cent vinyl chloride is used with an average molecular weight of about 15,000-16,000.

This brings us to Vinyon, the new textile fiber.

In making the multifilament yarn, the raw copolymer in the form of a white powder is dispersed in acetone to get a dope containing 23 per cent of the copolymer by weight. After filtering and deaerating the dope is spun the same as acetate by the dry or air spinning process.

After conditioning on the take-up bobbins the yarn is wet twisted to avoid static with 6 turns per inch whereupon it is given a stretch of over 100 per cent of its original length.

As in the case of nylon this stretching is a vital part in producing a good yarn so as to give it the high tensile strength and true elasticity. The stretched yarn is then set by immersion in water at 150° F. for several hours, after which it is ready to be wound to cones or skeins as the case may be.

The ordinary yarn is bright but may be dulled by incorporating finely ground pigments in the spinning dope just as is done in the case of viscose or acetate.

The tenacity may be controlled within a range of 1.00 to 4.00 grams per denier and the elongation correspondingly from 120 per cent to 18 per cent, the higher strength corresponding to the lower extensibility and vice versa. Being

Data on Vinyon



extremely water repellent the tenacity and extensibility of the dry and wet yarn are the same. For convenient comparison we give the following table:

| | Dry | | Wet | |
|---|---|---|---|---|
| | *Tenacity* | *Elongation* | *Tenacity* | *Elongation* |
| Degummed silk. | 4.22 | 16% | 3.40 | 26% |
| Viscose ..... | 2.00 | 18 | 1.00 | 28 |
| Acetate ..... | 1.40 | 27 | 0.85 | 36 |
| Vinyon No. 1.. | 4.00 | 18 | 4.00 | 18 |
| Vinyon No. 2.. | 2.30 | 25 | 2.30 | 25 |
| Vinyon No. 3.. | 1.00 | 120 plus | 1.00 | 120 plus |

A tenacity of 4.00 grams per denier expressed in another way is 77,200 pounds per square inch which corresponds to the strength of machinery or forging steel.

Although the yarn is quite water resistant as the table shows, the surface is readily wet out by the use of wetting agents although it is thermoplastic and softens at temperatures above 150° F. it does not support combustion, but if heated hot enough will burn with a very smoky flame.

During textile processing it is well to run with rather high humidity because of the static which develops. The knitting properties are very good indeed, for Vinyon due to its high strength and elasticity can be knit under higher tension thus producing a tighter stitch than is possible with other fibers.

The yarn and fabrics are in no way affected by water and are exceptionally resistant to acids and alakalis. Aqua regia, 70 per cent nitric, hydrochloric and even hydrofluoric acid of maximum concentration do not attack it at room temperature. The same is true of caustic soda or potash.

The lower aliphatic ketones like acetone, dissolve it as do some of the halogenated hydrocarbons. In contact with di-ethyl ether or the lower aromatic hydrocarbons it tends to swell; but it is unaffected by alcohol, gasoline and other aliphatic hydrocarbons. Vinyon is not attacked by bacteria, molds or fungi and will not support their growth. It does not conduct electricity and as water does not affect it, is an excellent insulator. Its high insulating power is shown by the ease with which it develops and retains the static charge. Its flexing strength and its stability to sunlight are excellent.

Dyeing of Vinyon seemed at first to offer some difficulty but this matter is well on the way to solution as a whole range of colors are already available. The yarn itself can, of course, be colored with pigments by incorporating these in the resin dispersion prior to spinning just as is done when the yarn is to be a dull yarn.

One way of dyeing the yarn is to use a bath containing solvents and non-solvents for the resin which temporarily swell the filaments. Another way is by means of many types of dyes using standard dyeing procedure modified, of course, as to temperature and by the use of a suitable dispersing agent for the dye. Still another way is to use oil soluble dyes applied from hydrocarbon baths.

Vinyon is at present being made in the following sizes and filament counts:

| *Denier* | *Filament* | *Price* |
|---|---|---|
| 60 | 46 | 1.80 |
| 120 | 92 | 1.65 |
| 180 | 138 | 1.50 |
| 250 | 184 | 1.45 |
| In the unstretched state: | | |
| 180 | 46 | 1.35 |

Small amounts of staple have been made which are being tried out for various purposes. Uses which have been suggested for Vinyon are the following:

Filter fabrics, fish lines, nets, seines, electric insulation, shower curtains; bathing suits, waterproof clothing, acid and alkali resistant clothing, fireproof awnings and curtains, upholstery, fusible shape-retaining fabrics and hosiery.

The staple fiber of Vinyon blended with natural fibers like cotton or wool, or with rayon, can be made into fabrics which will retain a pressed shape, fold or crease.

These are but a few of the uses which are suggested for this remarkable new textile fiber.

There is one thought to be kept in mind with respect to this paper. The figures given here, while true at the time, should be viewed with some latitude, due to the fact that experimental work in all the various processes involved is still being done.

In closing I wish to express my appreciation to the research staff of the Carbide & Carbon Chemical Corporation under Dr. E. W. Rugeley and especially to S. D. Douglas who very kindly placed much of the data here presented at my disposal in the preparation of this talk.

## DISCUSSION

*Dr. Schmidt*: I would like to start the ball rolling. Can you tell us the specific gravity as compared to the others, and also whether your unstretched and your stretched fibers have a different specific gravity or not?

*Dr. Bonnet*: I can't answer as to the specific gravity of the unstretched fiber; the stretched fiber has a specific gravity practically the same as acetate rayon, about 1.3. Nylon has a specific gravity of about 1.14 with viscose rayon about 1.5.

*Mr. Lindsly*: Will this Vinyon weave without slashing?

*Dr. Bonnet*: I would refer this question to Mr. Luttge.

*Mr. Luttge*: Those filter fabrics were woven without any warp sizing and some lighter fabrics with higher twist warpings have been woven without sizing.

*Dr. Bonnet*: They either have to have high twist or sizing of some kind, otherwise you tend to fuzz up the filaments and then there is difficulty in weaving.

*Mr. Borghetty*: In the copolymers, are the vinyl chloride or vinyl acetate intimately mixed chemically or only physically?

*Dr. Bonnet*: The monomer vinyl chloride and the mono-

mer of the acetate are mixed in the proportion of say 95 per cent of the chloride and 5 per cent of the acetate. Then the catalyzer is added—and the mixture subjected to the catalyzing action, so that copolymerization takes place simultaneously. If on the other hand you take the polymerized chloride and the polymerized acetate and start to mix those, you don't get anything, worth while. That is why it may be said that the vinyl acetate plasticizes internally the vinyl chloride.

*Mr. Dogin*: In coloring and dissolving an oil color in a hydrocarbon, is there a natural affinity between the fiber and the color, and if not, isn't there a danger of crocking, or rubbing after it is colored?

*Dr. Bonnet*: You are getting to a subject on which I am a little shaky, as I haven't done very much of that work myself. I think your idea on that is probably quite correct. These samples will not crock. They do not rub, nor will you find that these stockings will lose their color by being washed. These stockings happen to be new, but, there have been some which have been worn in the usual way and have been washed repeatedly about a dozen or more times that I know of. I don't know how many more times since then, but they look just the same as these stockings here. They seem not to have lost any color whatsoever. You understand that they have not only been washed, but that they have been worn in between washings.

I can't give you any details in the matter of dyeing as this is still in the experimental stage, to find the best way to do it. I have indicated in this paper simply suggestions.

*Mr. Winter*: You obtain this parchment-like fabric if you treat it at a higher temperature. I wonder whether this parchment is stable, or whether, with another treatment at the same temperature, or another treatment later on, it will change and get some other properties.

*Dr. Bonnet*: So far as I know, the material is extraordinarily stable to temperature changes, once you have fixed it. For example, all this yarn has been, we will say, fixed at a temperature of 150 degrees, or slightly above that. It is stable up to that temperature of setting. As soon as you heat it beyond that, then you begin to get shrinkage again. So far as the resin itself goes, it is quite stable.

*Mr. Winter*: If you put it in the same solvent once more and expose it to the solvent for a longer time, would that give any difference in the shrinkage?

*Mr. Luttge*: It depends on room temperature.

*Mr. Benzing*: You have a piece of paper there which was coated. Could you coat a fabric with that and still have the properties of Vinyon?

*Dr. Bonnet*: Yes, in a way. For example, for shower curtains, you can take an ordinary rayon fabric and coat it with the resin and impress a moire on it, at the same time making it perfectly waterproof.

*Mr. Benzing*: Would it add elasticity to the cloth?

*Dr. Bonnet*: I don't think so.

*Dr. von Bergen*: How does Vinyon take care of the body perspiration?

*Dr. Bonnet*: At the present time we are not interested in any fabrics for apparel use or anything of that sort. It doesn't absorb moisture, which includes perspiration.

*Dr. von Bergen*: A bathing suit would be quite close.

*Dr. Bonnet*: Since the fiber does not absorb water it dries quickly and therefore should feel warm in a short time.

*Dr. Wolf*: Dr. Bonnet, you indicated that oil soluble colors are suitable for dyeing. Do you know of any other colors?

*Dr. Bonnet*: No, I don't. I have just given you a general idea, that some of these oil soluble dyes have been found to color and dye some of this Vinyon. But, as I say, there is still a great deal of work to be done on the matter of dyeing to determine the types of dyes best suited for the purpose, the same as was the case with acetate rayon in its early days.

*Dr. Wolf*: So far, the oil colors are the only ones that are suitable?

*Dr. Bonnet*: Now you are putting me on the spot. I can't answer that. I asked Meadville to kindly give me some dyed Vinyon, and they sent me these five colors. They didn't say they had any more colors, or that that was all they had time for after I asked for them. However, that is what I got. I haven't asked them to tell me how they have dyed them, nor anything further about them. In fact, to tell you the truth, I didn't come here to tell you anything about it. (Laughter.)

*Mr. Black*: At what temperature were those stockings dyed?

*Dr. Bonnet*: Below 150 degrees; probably 140 degrees Fahrenheit.

*Mr. Oberer*: Being in the dry cleaning business, I must confess I see this new invention with certain misgivings, since you have already mentioned that some chlorinated solvents are harmful. Could you elaborate a little more, as a kind of a warning, along the lines of which solvents are harmful?

*Dr. Bonnet*: Many of the chloride hydrocarbons—for example, carbon tetrachloride—will swell the fiber, but they won't dissolve it. Take another case: If you found a spot on some fabric and tried to remove it with acetone, it would be just too bad—just about as bad as it would be with acetate rayon. I think in some dry cleaning ethylene dichloride is used. That substance would not help out the Vinyon either. But as already pointed out we are not at present interested in Vinyon for dress fabrics.

*Mr. Oberer*: How about steaming?

*Dr. Bonnet*: You couldn't steam it either. These fabrics would have to be done under 150 degrees. We are trying to control the uses of the yarn very carefully, so that it

will not run into some of these dry cleaning troubles that you anticipate.

*Mr. Mauersberger*: Dr. Bonnet, have you done any twist? How does it react under twist? Do those stockings contain yarn which has been twisted?

*Dr. Bonnet*: Those stockings have been twisted. So far as the textile end goes there is no trouble at all. It is quite similar to acetate rayon, and both have static problems.

*Mr. Mauersberger*: In other words, it wouldn't have any creping qualities, such as viscose would have?

*Dr. Bonnet*: Not unless you heated it above 150° F., then you might get certain creping qualities out of this yarn.

*Mr. Espelin*: If this particular fiber doesn't absorb water and if it doesn't absorb perspiration, won't these stockings be rather cold to wear in the wintertime?

*Dr. Bonnet*: I have seen girls and young ladies standing on street corners these cold days when their legs were purple from the cold and I was quite sure they were not wearing Vinyon nor nylon stockings, but most likely silk. Women's stockings must be sheer and are certainly not worn for warmth.

*Dr. Wolf*: In connection with this swelling, are there any water or alcohol soluble solvents that swell the fibers?

*Dr. Bonnet*: No, neither water nor alcohol affect it at all.


*Twentieth*

# ANNUAL MEETING AND CONVENTION

## HOTEL COMMODORE

## NEW YORK CITY

## OCTOBER 18TH AND 19TH, 1940

*General Chairman*

**PATRICK J. KENNEDY**

REGISTRATION COMMITTEE

J. H. Hennessey

Paul J. Luck

Leonard G. Tubbs

*Auspices of*

**NEW YORK SECTION**

**GEORGE L. BAXTER**
**Chairman, Registration Committee**

MANY years of activity as a member of the New York Section and his position as assistant Sales Manager of the Bradford Dyeing Association have given George L. Baxter a wide and intimate contact in the dyeing and finishing field. At the twentieth annual meeting he will be chairman of the registration committee. He has successively held the offices of chairman of the program committee, vice-chairman and chairman of the New York Section and at present is a councilor. At the fourteenth annual meeting held in New York in 1934 he was chairman of the reception committee. The names of the members of Mr. Baxter's committee appear at the left.

## Combination of

# Wool Protein with Acid and Base

*(Continued from page 107)*

high accuracy prevails up to this value, even in the presence of wool. Measurements between pH 6 and 9 required almost continuous flushing of the electrode vessel, and are less certain. pH values for solutions containing potassium hydroxide in concentrations of 0.1 *M* or more were calculated from their titers, allowance being made for the contribution to the titer of any hydrosulfide present. Acid solutions with an ionic strength of more than 0.1 required application of a small empirical correction (between 0.02 pH at ionic strength 0.2 and 0.11 pH at ionic strength 1.0) due to the difference in ionic strength between the standardizing buffers and the solutions measured.

(*d*). *Control of Temperature*—A well-stirred 200-liter water-thermostat equipped with cooling coils, 300-watt heating element, mercury thermoregulator, and time-delay relay, kept the temperature constant at 25.00° ± .02° C. No thermoregulator was used at 0° C.; ice was allowed to form on the coils as the result of intermittent operation of the cooling unit. With a large amount of ice present, the temperature remained constant to ± .01° C.

## III. RESULTS AND DISCUSSION

### 1. Combination with Hydrochloric Acid

Measurements of the combination of wool with hydrochloric acid as a function of pH at 0° C. are given in Table 1, in which each section, except the first, summarizes data obtained at a different constant ionic strength. In the first section each measurement represents a different ionic strength since no salt was added. Data obtained both by titration of acid and of chloride are given. As was to be expected from considerations of electrical neutrality, the values in the two columns agree very closely. This agreement shows that the small amount of alkaline ash in the material used in most of the experiments neutralizes only negligible amounts of acid. In those cases in which much ash was known to be present, the agreement demonstrates the adequacy of the corrections applied for the effect of this ash*.

The measurements of acid bound (Table 1) are represented graphically in Figure 2, in which the continuous curves serve to differentiate the sets of points from one another. All of the other curves shown are distinguished from the "no-salt" curve (at the extreme left of the figure) by their smaller slopes. When compared at a point well above the base line, as, for example, at the points at

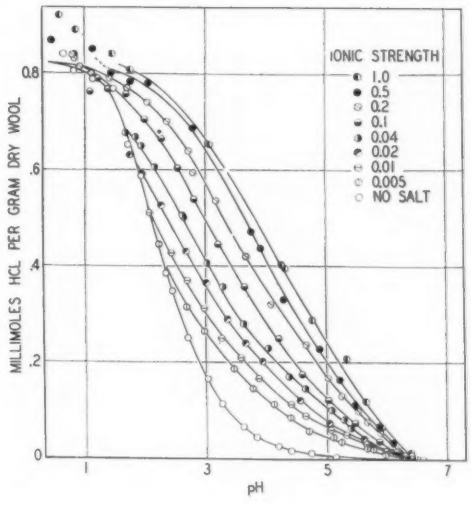



**Figure 2. The combination of acid by wool as a function of pH and ionic strength at 0°. (To avoid crowding the figure, only a single set of the experimental values obtained at an ionic strength of 0.2 is included. The smooth curves serve merely to distinguish the sets of data from one another.)**

which half the maximum acid-binding capacity is found, the slopes of all of them are very nearly equal. Near the base line the slopes vary as the curves converge and finally cross†. The addition of even small amounts of salt suffices to produce this difference: thus, when compared at 0.05 millimole of acid bound per gram, the point on the curve obtained with a total ion concentration of only 0.005 is shifted with respect to a corresponding point on the no-salt curve by about 1.3 pH units. The magnitude of this effect may be made clearer by comparing the amounts of acid bound at the same pH. In the absence of salt, only a little more than 0.01 millimole of acid per gram is bound at pH 4.6, but the addition of salt, sufficient to bring the concentration of chloride to 0.005 *M*, increases this figure almost six-fold. At pH 5 and above, this factor is even larger. Conversely, as the part of the total ionic strength which is contributed by salt diminishes, the factor becomes smaller, and each curve finally terminates at its intersection with the curve obtained without salt.

A simple regularity relates the curves obtained with different total ionic strengths: the distance (with respect to pH) between any two adjacent curves, taken for convenience at the point of half of the maximum combination with acid, is only slightly less than the logarithm of the

*When alkaline ash is combined with wool, the chloride disappearing from solution rather than the decrease in titratable acidity is a measure of the acid which would be taken up by ash-free wool. Thus, curves of chloride bound as a function of pH, although of lower accuracy, require no adjustments for the presence of ash.

†The positions of the curves are reversed on the alkaline side of the point of zero combination and again tend to become parallel.

## TABLE 1

### Combination of Wool with Hydrochloric Acid at 0°

#### (a) NO ADDED SALT

| *pH* | *Acid Bound Millimoles per g.* | *Chloride Bound Millimoles per g.* |
|---|---|---|
| *0.447 | 0.868 | ..... |
| 0.635 | 0.838 | ..... |
| *0.792 | 0.836 | 0.810 |
| 0.813 | 0.805 | 0.804 |
| *0.814 | 0.829 | 0.836 |
| *0.918 | 0.813 | ..... |
| *1.087 | 0.762 | 0.771 |
| 1.125 | 0.789 | 0,736 |
| 1.470 | 0.768 | 0.754 |
| *1.663 | 0.676 | 0.694 |
| 1.711 | 0.652 | 0.654 |
| *1.741 | 0.631 | 0.635 |
| 1.931 | 0.574 | 0.585 |
| *2.061 | 0.510 | 0.515 |
| 2.228 | 0.445 | 0.440 |
| *2,340 | 0,385 | 0.399 |
| 2.451 | 0.348 | 0,353 |
| 2.726 | 0.251 | 0.261 |
| 3.039 | 0.166 | 0.169 |
| 3.272 | 0.114 | 0.113 |
| 3.620 | 0.067 | 0.071 |
| 3.845 | 0.045 | ..... |
| 4.198 | 0.027 | 0.023 |
| 4.414 | 0.017 | 0.023 |
| 4.740 | 0.012 | 0.018 |
| 5.145 | 0.004 | 0.009 |

#### (b) IONIC STRENGTH 0.005

| *pH* | *Acid Bound Millimoles per g.* | *Chloride Bound Millimoles per g.* |
|---|---|---|
| 2.340 | 0.385 | 0.399 |
| 2.681 | 0.314 | 0.324 |
| 2.980 | 0.264 | 0.263 |
| 3.469 | 0.187 | 0.193 |
| 3.778 | 0.146 | 0.143 |
| 4.130 | 0.113 | ..... |
| 4.403 | 0.085 | 0.088 |
| 4.701 | 0.058 | 0.073 |
| 5.108 | 0.045 | 0.046 |
| 5.236 | 0.035 | 0.039 |
| 5.670 | 0.022 | 0.024 |
| 5.769 | 0.021 | 0.019 |
| 5.96 | 0.009 | ..... |
| 6.5 | 0.000 | ..... |

#### (c) IONIC STRENGTH 0.01

| *pH* | *Acid Bound Millimoles per g.* | *Chloride Bound Millimoles per g.* |
|---|---|---|
| 2.061 | 0.510 | 0.515 |
| 2.442 | 0.427 | 0.427 |
| 2.705 | 0.369 | 0.368 |
| 2.982 | 0.312 | 0.313 |
| 3.326 | 0.250 | 0.266 |
| 3.593 | 0.209 | 0.221 |
| 3.856 | 0.167 | 0.167 |
| 4.412 | 0.113 | 0.118 |
| 4.652 | 0.089 | 0.095 |
| 5.072 | 0.061 | 0.079 |
| 5.317 | 0.050 | 0.059 |
| 5.649 | 0.032 | 0.043 |
| 5.98 | 0.017 | 0.021 |
| 6.41 | 0.008 | ..... |
| 6.5 | 0.000 | ..... |

#### (d) IONIC STRENGTH 0.02

| *pH* | *Acid Bound Millimoles per g.* | *Chloride Bound Millimoles per g.* |
|---|---|---|
| 1.741 | 0.631 | 0.635 |
| 1.950 | 0.591 | 0.621 |
| 2.265 | 0.525 | 0.525 |
| 2.675 | 0.429 | 0.429 |
| 3.017 | 0.365 | 0.366 |
| 3.368 | 0.289 | 0.295 |
| 3.668 | 0.240 | 0.238 |
| 3.945 | 0.202 | 0.204 |
| 4.563 | 0.121 | 0.118 |
| 5.048 | 0.074 | 0.080 |
| 5.622 | 0.042 | 0.047 |
| 6.4 | 0.000 | ..... |

#### (e) IONIC STRENGTH 0.04

| *pH* | *Acid Bound Millimoles per g.* | *Chloride Bound Millimoles per g.* |
|---|---|---|
| 1.663 | 0.676 | 0.694 |
| 1.830 | 0.668 | 0.675 |
| 1.925 | 0.650 | 0.678 |
| 2.152 | 0.605 | 0.616 |
| 2.620 | 0.505 | 0.494 |
| 2.639 | 0.500 | 0.494 |
| 3.016 | 0.406 | 0.400 |
| 3.294 | 0.357 | 0.382 |
| 3.628 | 0.280 | 0.319 |
| 4.035 | 0.229 | 0.222 |
| 4.377 | 0.171 | 0.193 |
| 4.650 | 0.146 | 0.140 |
| 5.080 | 0.102 | 0.102 |
| 5.283 | 0.082 | 0.082 |
| 5.40 | 0.064 | 0.063 |
| 6.3 | 0.000 | —0.011 |

#### (f) IONIC STRENGTH 0.1

| *pH* | *Acid Bound Millimoles per g.* | *Chloride Bound Millimoles per g.* |
|---|---|---|
| 1.087 | 0.762 | 0.771 |
| 1.201 | 0.789 | 0.794 |
| 1.380 | 0.767 | 0.776 |
| 1.678 | 0.745 | 0.740 |
| 1.988 | 0.704 | ..... |
| 2.269 | 0.664 | 0.680 |
| 2.535 | 0.603 | ..... |
| 2.810 | 0.538 | 0.510 |
| 3.206 | 0.446 | ..... |
| 3.650 | 0.357 | ..... |
| 4.210 | 0.250 | ..... |
| 4.617 | 0.176 | 0.195 |
| 5.032 | 0.122 | ..... |
| 5.473 | 0.075 | ..... |
| 5.867 | 0.037 | ..... |
| 6.15 | 0.016 | ..... |
| 6.3 | 0.008 | ..... |
| 6.4 | 0.003 | ..... |
| 6.5 | 0.000 | ..... |

#### (g) IONIC STRENGTH 0.2

| *pH* | *Acid Bound Millimoles per g.* | *Chloride Bound Millimoles per g.* |
|---|---|---|
| 0.792 | 0.836 | 0.810 |
| †0.814 | 0.829 | 0.836 |
| ‡0.918 | 0.813 | ..... |
| 1.100 | 0.799 | 0.788 |
| ‡1.130 | 0.798 | 0.828 |
| §1.400 | 0.789 | ..... |
| 1.409 | 0.788 | 0.773 |
| ‡1.433 | 0.774 | 0.780 |
| 1.707 | 0.770 | 0.756 |
| ‡1.751 | 0.753 | 0.775 |
| †1.982 | 0.730 | 0.730 |
| 2.038 | 0.740 | 0.756 |
| ‡2.061 | 0.702 | 0.759 |
| 2.364 | 0.701 | 0.712 |
| ‡2.378 | 0.670 | ..... |
| 2.708 | 0.641 | ..... |
| ‡2.744 | 0.595 | ..... |
| §2.790 | 0.594 | ..... |
| 3.172 | 0.535 | 0.591 |
| ‡3.273 | 0.487 | ..... |
| †3.571 | 0.435 | ..... |
| 3.670 | 0.419 | 0.460 |
| ‡3.825 | 0.372 | ..... |
| 4.082 | 0.320 | 0.294 |
| †4.359 | 0.279 | 0.300 |
| 4.662 | 0.224 | 0.198 |
| ‡4.855 | 0.177 | ..... |
| 5.015 | 0.168 | ..... |
| 5.246 | 0.131 | 0.120 |
| ‡5.400 | 0.112 | ..... |
| 5.528 | 0.099 | 0.085 |
| ‡5.564 | 0.067 | ..... |
| 5.670 | 0.078 | ..... |
| 5.887 | 0.054 | ..... |
| ‡5.94 | 0.030 | ..... |
| 6.14 | 0.023 | ..... |
| ‡6.3 | 0.002 | ..... |
| 6.5 | 0.002 | ..... |
| ‡6.7 | —0.027 | ..... |
| 6.97 | —0.048 | ..... |
| ‡7.0 | —0.041 | ..... |

| (h) IONIC STRENGTH 0.5 | | (i) IONIC STRENGTH 1.0‖ | |
|---|---|---|---|
| *pH* | *Acid Bound millimoles per g.* | *pH* | *Acid Bound millimoles per g.* |
| 0.447 | 0.868 | 0.578 | 0.920 |
| 0.832 | 0.838 | 0.840 | 0.890 |
| 1.130 | 0.850 | 1.138 | 0.852 |
| 1.438 | 0.799 | 1.445 | 0.840 |
| 1.745 | 0.784 | 1.743 | 0.794 |
| 2.048 | 0.781 | 2.062 | 0.777 |
| 2.780 | 0.687 | 3.074 | 0.652 |
| 3.750 | 0.471 | 4.258 | 0.403 |
| 3.910 | 0.432 | 4.334 | 0.395 |
| 4.304 | 0.330 | 4.768 | 0.288 |
| 4.887 | 0.228 | 5.342 | 0.208 |
| 5.211 | 0.164 | 5.651 | 0.119 |
| 5.472 | 0.112 | 5.908 | 0.065 |
| 5.870 | 0.068 | 6.4 | 0.013 |
| 6.10 | 0.034 | 6.7 | —0.015 |
| 6.5 | 0.002 | 7.0 | —0.048 |

*No-Salt data for experiments at constant ionic-strengths in other columns. †, ‡, §Supplementary control determinations on batches containing alkaline ash. These data are corrected for differences in ash as explained in the text. ‖Data in this column corrected for alkaline ash of wool used.

ratio of the ion concentrations which the curves represent. This implies a close approach to a direct stoichiometric relationship of the acid bound by wool to the concentration of chloride ion as well as to the concentration of hydrogen ion; thus, each time the chloride concentration is doubled, the curves are shifted to pH values approximately 0.30 unit higher than those at the lower ionic strength. As shown in Figure 3, this direct relation is approximated very closely over the forty-fold range of chloride concentrations between 0.005 and 0.200 *M*. Above this range the dependence on ionic strength diminishes: it appears that the curves may approach a limiting position with respect to the pH axis, and that this limit may not be far beyond the position of the curve at 1.0 *M* ionic strength. It is significant that the pH for half maximal combination (4.2) which characterizes the position of the curve at 1.0 *M* chloride is practically identical with the mid-point of the first S-shaped portion of the titration curves of soluble proteins measured at the same salt concentration.

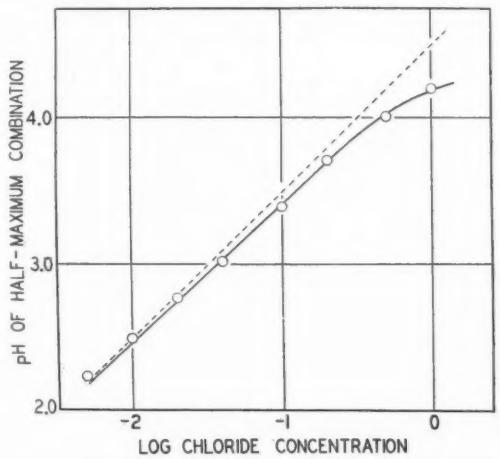



**Figure 3. The dependence of the pH of half-maximal combination with acid on the level at which the chloride concentration is held constant. The broken line represents a direct stoichiometric relation.**

The remarkably regular dependence of the positions of the curves on the total concentration of chloride ions may be interpreted as implying a certain degree of interchangeability of the concentrations of acid and salt or of hydrogen and chloride ions as factors limiting the amounts of acid bound. The function which describes the amount of acid bound must involve two independent variables, and its dependence on each of these variables must possess a degree of similarity. Thus if, instead of plotting the amount of acid bound against pH, it were plotted against the negative logarithm of the total chloride concentration at a number of constant concentrations of acid, a group of curves would be obtained related to one another very much as the curves in Figure 2. Several earlier studies on *soluble* proteins[4, 10] have shown the existence of much smaller effects of salt on the positions and shapes of their acid-titration curves. These effects are only slightly larger than those which characterize the common buffers, and which are explained in terms of the modern electrical-interaction theory of solutions. They cannot be compared to the much larger and nearly stoichiometric dependence which is found with wool in the range of low ionic strengths. The significance of this large and interchangeable dependence of acid and salt on acid combination is discussed in Section IV of this paper.

Since the curves of acid combination as a function of pH represent the reaction of hydrogen ions with carboxylate ions (see footnote *, page 104) and since the dissociation constants of the conjugate carboxylic acids have only a slight dependence upon temperature (between 0° C. and room temperature) the effect of temperature on these curves should be small. This expectation is completely fulfilled by comparison of the data at 0° already given with the measurements on wool at 25° C. summarized in Table 4 and plotted in Figures 1 and 5*. Comparison of the data obtained in the absence of salt at either temperature with the data of Speakman and Stott[45], obtained at an intermediate temperature, is therefore not unjustified. The agreement with the data of these investigators is close over the greater part of their range, and is probably within the limits of possible differences in definition of the pH scale in the two investigations. Although different wools were used, there is also close agreement between the values for maximum acid-binding capacity. As shown in Figure 2, all of the sets of points tend to level off near pH 1 at 0.80 to 0.84 milliequivalent of acid bound per gram†. Speakman obtained a maximum

*A closer study of the effects of temperature on combination with acid and base is in progress. These effects are of importance in the application of the low-temperature titration data presented in this paper to such related aspects of wool processing as dyeing and scouring, which usually involve high temperatures.

†The slight differences in the maxima shown by the various curves may represent, in part, residual differences in alkaline ash for which inadequate corrections have been made. It is more likely that they are the result of incorrect allowance for differential absorption of water, salt, and acid when wool unsaturated with water is placed in the various solutions. This absorption will affect only the values calculated for the most acid solutions. It is also possible that in the most acid solutions, the titration of the very weakly basic amide groups is begun, and that the curves are not entirely level below pH 0.7.

of 0.80 or 0.81 with wool which had been previously extracted with very dilute hydrochloric acid to remove the ash. The agreement of our maximum values with his supports the previous conclusion that the residual 0.10 per cent of ash in the wool used in the present investigation is practically without effect on the measurements. This conclusion is also borne out by the amounts of acid shown to be bound in the absence of salt at pH 4.8, which Speakman considers to be the point of zero combination. This quantity, approximately 0.01 millimole per gram, is therefore the maximum amount which may be attributed to ash present in the wool of the present investigation. The effect of this ash in neutralizing acid may be even smaller, or zero, since Speakman's acid extraction and adjustment to pH 4.8 may have resulted in the combination of so small an amount of acid as 0.01 millimole with his wool. The curves obtained in the presence of salt make plain that pH 4.8 is not the point of zero combination of acid with wool at 0° C. It seems probable that at this temperature the base line is crossed, not only in the presence of salt but in salt-free solutions as well, at pH 6.3-6.5.

### 2. Combination with Potassium Hydroxide

Although fewer measurements of the combination of wool with base have been made, they suffice to show that the relationships between the data on acid combination obtained in the presence and absence of salt, and at different constant ionic strengths, also prevail in the alkaline branches of the wool titration curves. Very little modification of the foregoing description is therefore necessary. The corrected data for base combination at 0° C., at two ionic strengths and in the absence of added salt, are summarized in Table 2. Parallel data for the combination of the fiber with potassium ion, obtained by electrodialysis, are omitted from this table; although less accurate than the data for base bound, they are in fair agreement with the values given. In Figure 4, the data of Table 2 are shown combined with the corresponding sets of measurements for acid combination; the figure thus represents the complete titration curve under these conditions over the entire pH range studied.

When the data obtained at constant ionic strengths are so presented in their entirety, the composite curves bear a close resemblance to the titration curves of dissolved proteins. The acid branch crosses the base line without discontinuity and continues downward with progressively more gradual slope until buffering capacity is practically lost over a range of 1 to 2 pH units. Approximately 0.10 millimole of base per gram has been bound at this point. As the pH increases, marked buffering capacity once more appears and large amounts of base are bound in the pH range 11-14. The largest amount bound in the range measured is 0.78 millimole per gram, but there is no indication from the shape of the curves that somewhat larger amounts of base would not be bound at a higher pH. This maximum value is slightly higher than that reported by Harris and Rutherford. The cause of part of this

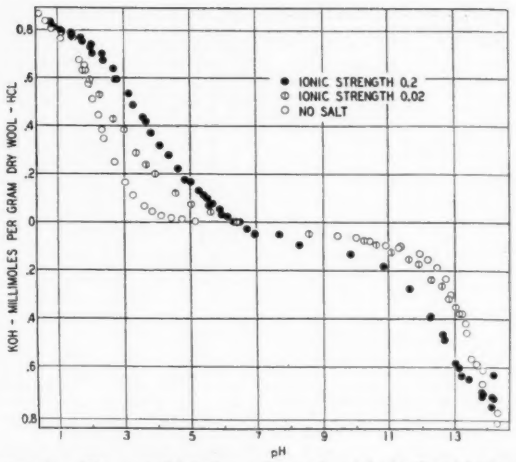



**Figure 4. The combination of wool with hydrochloric acid and with potassium hydroxide as a function of pH. Data are shown obtained in the absence of added salt, and in the presence of two different constant total ionic concentrations.**

**TABLE 2**

**Combination of Wool with KOH at 0°***

| (a) NO ADDED SALT | | (b) IONIC STRENGTH 0.02 | | (c) IONIC STRENGTH 0.20 | |
|---|---|---|---|---|---|
| *pH* | *Base Bound Millimoles per g.* | *pH* | *Base Bound Millimoles per g.* | *pH* | *Base Bound Millimoles per g.* |
| ‡ 9.45 | 0.055 | 8.59 | 0.047 | † 6.95 | 0.050 |
| ‡10.01 | 0.063 | 10.25 | 0.095 | 7.68 | 0.050 |
| ‡10.43 | 0.077 | 10.62 | 0.112 | 8.28 | 0.093 |
| ‡10.91 | 0.094 | 11.09 | 0.142 | 9.84 | 0.130 |
| 11.32 | 0.105 | 11.60 | 0.170 | 10.83 | 0.180 |
| 11.37 | 0.097 | 11.90 | 0.191 | 11.63 | 0.273 |
| 11.93 | 0.128 | 12.27 | 0.236 | †12.23 | 0.391 |
| 12.17 | 0.153 | 12.60 | 0.262 | 12.25 | 0.389 |
| 12.46 | 0.185 | 12.81 | 0.316 | 12.62 | 0.462 |
| 12.72 | 0.232 | 13.03 | 0.348 | 12.68 | 0.495 |
| 12.88 | 0.297 | 13.22 | 0.397 | 13.01 | 0.582 |
| 13.12 | 0.375 | | | †13.11 | 0.600 |
| ‖13.22 | 0.397 | | | 13.19 | 0.635 |
| 13.32 | 0.436 | | | †13.39 | 0.649 |
| 13.35 | 0.476 | | | ‡13.82 | 0.704 |
| 13.49 | 0.565 | | | §13.82 | 0.722 |
| ‡13.65 | 0.586 | | | †13.85 | 0.710 |
| 13.68 | 0.590 | | | ¶14.11 | 0.764 |
| 13.85 | 0.669 | | | ‡14.13 | 0.723 |
| ‡13.85 | 0.611 | | | †14.16 | 0.630 |
| 14.11 | 0.764 | | | §14.17 | 0.730 |
| ‡14.13 | 0.723 | | | | |
| †14.16 | 0.630 | | | | |
| §14.17 | 0.730 | | | | |
| 14.29 | 0.828 | | | | |
| ‡14.30 | 0.787 | | | | |

*The data are corrected for the effects of decomposition and for their content of alkaline ash, as explained in Section II.
†, ‡Supplementary control determination on different conditioning batches, and with different periods of equilibration.
§Control determination on wool of different ash content.
‖Data from column (b).
¶Data from column (a).

difference has already been given (see Section II). Another part may be due to the alkaline ash content of the wool yarn, as pointed out in the earlier work.

Although the alkali titration curve is more complex than that of the acid curve, the shifts produced in its position by salt are exactly analogous to the shifts in the acid curves. Thus, every point on the curve representing measurements at 0.02 *M* is shifted to the alkaline side by

almost exactly 1.0 pH unit from the corresponding point at 0.20 *M*. The data obtained without salt are widely separated from the others, especially as the pH for zero combination is approached. The curve representing the data obtained in the absence of salt in both alkaline and acid solutions consists of two steep sections and shows clearly the long central region of about 5 pH units in which the amounts of acid or base bound are very small.

### 3. Relations to Titration Curves of Soluble Proteins

The occurrence of a large and nearly stoichiometric dependence of the pH coordinate of the titration data for wool on the ionic concentration makes it of some interest to determine whether any of the large number of possible positions of the resulting curves corresponds with the curve which would characterize a similar protein in the dissolved state. It has been shown (Figure 1) that the acid curves of wool and of a comparable soluble protein, egg albumen, obtained in the total absence of salt, differ very widely. In Figure 5, data for the same two proteins are compared at a high salt concentration, 0.5 *M*. Above this concentration the positions of the titration curves with respect to the pH axis have a lower degree of dependence on salt concentration*.

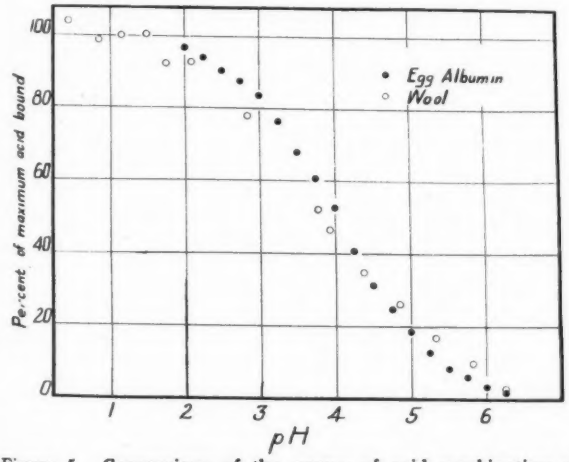



**Figure 5. Comparison of the curves of acid combination of wool and of egg albumin at 25°, in the presence of 0.5 *M* chloride.**

The data for wool shown in Figures 1 and 5 were obtained at 25° C., the temperature used by Cannan, and are summarized in Table 3. The points for egg albumen in Figure 5 represent interpolations at equidistant points along the pH axis between the curves given by Cannan[4] for 0.27 and 0.67 *M* salt. The data for wool at 25° C. differ only slightly from those at 0° already described.

It is clear that the differences between the data for the two proteins, so marked in Figure 1, have been greatly reduced in Figure 5. Aside from a slightly more acid position for the curve for wool, discrepancies to which

*The smaller shifts that occur at salt concentrations above 0.5 M. are of practically the same magnitude as those which occur with the dissolved protein in the same range of concentrations.

**TABLE 3**
**Combination of Wool with Hydrochloric Acid at 25°***

| (a) NO ADDED SALT | | (b) IONIC STRENGTH 0.50 | |
|---|---|---|---|
| *pH* | *Acid Bound Millimoles per g.* | *pH* | *Acid Bound Millimoles per g.* |
| 0.638 | 0.877 | 0.412 | 0.877 |
| 0.826 | 0.802 | 0.839 | 0.810 |
| 1.448 | 0.687 | 1.154 | 0.815 |
| 1.710 | 0.599 | 1.470 | 0.824 |
| 1.915 | 0.520 | 1.774 | 0.757 |
| 2.191 | 0.402 | 2.088 | 0.762 |
| 2.406 | 0.316 | 2.835 | 0.636 |
| 2.722 | 0.225 | 3.772 | 0.426 |
| 3.093 | 0.143 | 3.929 | 0.383 |
| 3.370 | 0.087 | 4.380 | 0.281 |
| 3.962 | 0.036 | 4.852 | 0.214 |
| 4.603 | 0.014 | 5.33 | 0.140 |
| 5.257 | †—0.013 | 5.82 | 0.082 |
| 6.38 | †—0.026 | 6.25 | 0.023 |
| 6.82 | †—0.035 | 6.50 | 0.002 |
| 7.28 | †—0.042 | 6.72 | †—0.026 |

*The data are corrected for water uptake by the fiber and the effect of its alkaline ash as explained in Section II.
†Negative values indicate loss of bound acid or combination with hydroxyl ion.

significance may be attached appear only in the region of very slight acid binding. These discrepancies are very small. Some disagreement might be expected in this region owing to small differences between the ratios of imidazole to carboxyl groups in the two proteins. Since the histidine content of both proteins is small, it is very likely that the analytical values reported are not exact.

This comparison shows that proteins of comparable composition with respect to dicarboxylic amino acids and histidine, give closely similar acid-combination curves, when they are compared over the same acid range in solutions containing high concentrations of ions. This result must be taken into account in any explanation offered for the great difference in acid-binding behavior between the same proteins when neutral salts are absent. In itself, the comparison is sufficient to exclude from consideration explanations which appeal to a fundamental difference in configuration of the acidic and basic groups in the two classes of substances. The comparison gains further significance from Cannan's demonstration that the egg albumen curves of Figures 1 and 5 are very similar to those of polyvalent acids in which all of the dissociating groups have the same intrinsic strength, but in which the negative charges left by the dissociation of each hydrogen ion hinder the dissociation of the remaining groups. The present comparison indicates that Cannan's reasoning must apply to wool to the same degree as to egg albumen. The differences between the titration curves of the two proteins found in the absence of salt must find their explanation in elements of an equilibrium which occurs between two phases.

### 4. Analysis of the Titration Curves

By analogy with similar analyses of titration curves of soluble proteins[8, 9, 10, 27, 28] it should be possible to identify each portion of the curves for wool at high constant ionic strength with one of the several kinds of dissociating groups contributed by the constituent amino-acid residues. The acid branch is clearly attributable to the back-titrations of the ionized carboxyl groups of glutamic, hydroxy-

glutamic, and aspartic acids, overlapping in the pH range above 4.5 the combination with acid of the imino groups of histidine. In addition, those carboxyl groups which have not donated their protons to amino and guanidino groups (the excess of carboxyl groups over these groups) must be responsible for part of the unbroken continuation of this S-shaped curve to pH 8; another part is contributed by the removal of protons from those histidine residues which have their imino groups in the charged (acid) form. In the unbuffered region between pH 8 and 10 almost no groups dissociate, but in the buffered section of the curve (pH 11-14) the ε-amino groups of lysine are regenerated from their conjugate acid forms by loss of a proton. In addition, the hydroxyl groups of tyrosine (if they are free in wool) become ionized, and at least some of the guanidino groups of arginine, present in their conjugate acid form, give up their protons.

The foregoing partial analysis of the composition of the high ionic strength curves may be rendered more convincing by the following quantitative comparison of its implications with the admittedly incomplete data at present available on the amino-acid composition of wool.

**TABLE 4**

**Acidic and Basic Amino-Acids in Wool**

| | Ref. | Per Cent | *Millimoles per g.* |
|---|---|---|---|
| 1. Aspartic Acid | (46) | 7.27 | 0.545 |
| 2. Glutamic Acid | (46) | 15.27 | 1.035 |
| 3. Amide nitrogen | (46) | 1.37 | 0.978 |
| 1 plus 2 minus 3 | | | 0.602 |
| 4. Arginine | (16) | 10.2 | 0.586 |
| 5. Lysine | (39) | 3.3 | 0.226 |
| 6. Histidine | (50) | 0.66 | 0.044 |
| 4 plus 5 plus 6 | | | 0.856 |
| 1 plus 2 minus 3 plus 4 plus 5 plus 6 | | | 1.458 |
| 7. Tyrosine | (38) | 5.8 | 0.320 |

The sum of the acid-binding and base-binding capacities of wool between pH 0.8 and 14.3 is 1.59 ± .04 millimoles per gram. Table 4 lists the reported contents of aspartic and glutamic acids, histidine, lysine, arginine, amide nitrogen, and tyrosine. The sum of the acid- and base-binding equivalents, *omitting the tyrosine*, and after subtraction of the amide nitrogen to allow for the part of the dicarboxylic acids present as glutamine and asparagine, is 1.46 millimoles per gram. *With the tyrosine included* it is 1.78. Both figures are given because the experimental sum falls between them, and because there is a suggestion in certain unpublished data on wool and in published data on some soluble proteins[15, 47] that some or all of the hydroxyl groups of tyrosine in proteins may not be free to combine with base. Another explanation of the small discrepancy is possible: the figures for the carboxylic acids and histidine were obtained by isolation methods and are likely to be low. Should this be the case one may conclude that tyrosine hydroxyl groups are *not* titrated. However, it is not certain that the present measurements give the maximum base-binding capacity, and only part of the arginine may be combined with base at pH 14.3. Should this be true one may conclude that the tyrosine is titrated quantitatively.

It is possible to calculate roughly what the maximum base-binding capacity should be, from the maximum amount of acid which is bound and the pH at which no combination with either acid or base occurs. Since the latter falls in the titration range of histidine, which is present in small amount, it appears that in the uncombined state of the protein practically all the carboxyl groups have donated their hydrogen ions to basic groups. Thus the sum of the basic groups (from lysine and arginine) must be equal to the sum of the carboxyl groups (from glutamic, hydroxyglutamic, and aspartic acids) within a margin of uncertainty which is smaller than the small content of histidine. The maximum base-binding capacity, *excluding tyrosine*, should therefore correspond roughly with the maximum acid-binding capacity, — which may be taken as 0.82. The sum of the two should not be far from $2 \times 0.82 = 1.64$, a figure close to 1.59, the value found. It would be necessary to assume that about half the arginine is still not titrated at pH 14.3 in order to make room for the titration of all the tyrosine. This would increase the maximum amount of base bound at higher alkalinities to about 1.18, far above the figure found at pH 14.3. The balance of probability therefore favors the conclusion that in the unhydrolyzed wool, the hydroxyl groups of tyrosine are not free to combine with base, and therefore contribute no part of the large buffering effect at pH 11-14.

This conclusion entails the plausible assumption that some or all of the analytical data are low. Since the sum of the arginine and lysine listed in the table is 0.82 millimole per gram, in good agreement with the capacity of wool to bind acid, the largest part of the discrepancy must be sought in the values for the dicarboxylic acids and amide nitrogen, in both of which the potentialities for error have long been recognized. The relatively large amount of acid plus base combined between pH 6 and 8 (about 0.13 millimole) suggests that the histidine figure in Table 3 may also be low, since only a small part of the combination in this range may be attributed to carboxyl groups. However, an increase in the estimated histidine content will not greatly affect the close agreement of the experimentally determined sum of acid- plus base-binding capacity with the sum calculated from the acid-binding capacity alone, since only an indeterminate part of the histidine content contributes to the curve of acid combination, the balance being responsible for a part of the base combined at higher pH.

This analysis of the structure of the titration curve of wool differs in at least one significant respect from the interpretation offered by MacMahon and Speakman[36]. These authors regard the step on the curve which represents the base bound in salt-free solutions, between the pH at zero combination and the relatively unbuffered section at pH 8-10 as caused by the titration of sulfhydryl groups which are present in wool that has suffered partial decomposition. In the present investigation on undamaged wool,

this step on the curve of base-combination also appears; in the curves obtained in the presence of salt it clearly represents a continuation of the first S-shaped branch of the titration curve which begins its downward course near pH 1, and which has been accounted for above as an expression of the partially overlapping titration of carboxyl and imino groups. It seems unlikely that sulfhydryl groups, which are extremely weak acids, would be appreciably titrated in this range of pH. The formation of strongly acid groups by exposure to light may result in a shift of the pH at zero combination to lower values. This would have the effect of increasing the height of the alkaline step, which Speakman attributed to sulfhydryl.

***(To be concluded in next issue)***

## Technical Notes—

***(Concluded from page 108)***

From such observations it is deduced by the authors that the conception which regards the process of vat dyeing as an absorption, or combination of the leuco-dye and cellulose, the progress of which is conditioned by the relatively slow diffusion of the dye molecules to the interior of the cellulosic filament, is the most fruitful hypothesis which can at present be constructed.

Part 3 of the paper describes the measurements of exhaustion rate, degree of exhaustion and diffusion rate of a range of commercial vat dyes. The dyes are classified according to the results obtained, and the data correlated with the behavior of dyes in practice. The general nature of the vat dyeing process is revealed as having two phases —(1), absorption of the dye by part of the dyed material, which causes rapid exhaustion of the dye bath, and (2) a process of levelling, dependent for its speed on the ease of diffusion of the dye in viscose rayon.

Part 4 classifies a long list (81) of vat dyes according to their capacity to penetrate and give level dyeings. This involves use of a "strike" index determined for each dye, a symbol which serves to indicate the degree of difference (if any) in depth of shade found to exist between the outside and inside of a skein when removed from the bath, and the additional dyeing time required to level out any such inequality.

### The Commercial Use of Liquid Sulfur Dioxide in Textile Bleaching

*C. F. Ward—Jour. Soc. Dyers and Col.*, 55-9, *September*, 1939.—A description of a plant's experience in changing to the use of liquid sulfur dioxide in cylinders from the old method of burning sulfur in the stoves used in wool bleaching.

As originally employed, the stoves had always presented certain difficulties, not the least of which was the impossibility of keeping the surrounding atmosphere free from the fumes of $SO_2$. With the introduction of the liquefied product, most of these were obviated. The liquid was led from the cylinder onto a basin of suitable material and allowed to evaporate into a current of air drawn over the basin and into the bleaching chamber. Arrangements were made to warm the basin as required when the evaporating liquid tended to congeal from the rapid absorption of heat. It was found necessary to overhaul the stove chambers to be sure they were airtight. Waste gases were exhausted from the chambers through a specially designed scrubber, and final traces of $SO_2$ fumes neutralized by use of a waste lime sludge from the water softener.

# TRADE NOTES • NEW PRODUCTS

**• SALESMEN'S GOLF TOURNAMENTS**

Philip LoBue, Joseph Turner & Co., is chairman of the entertainment committee of the Salesmen's Association of the American Chemical Industry. He has announced the following dates for the four golf tournaments:

June 18th—Green Meadow Country Club, Harrison, N. Y.

July 16th—Canoe Brook Country Club, Summit, N. J.

August 20th—Bonnie Briar Club, Larchmont, N. Y.

September 17th—Pomonok Country Club, Flushing, L. I., N. Y.

Details will be announced later.

**• MEETING, S. C. I.**

A meeting of the Society of Chemical Industry was held on February 16th at the Cascade Ballroom of the Biltmore Hotel, New York City. Dr. Wallace P. Cohoe, Chairman of the American Section, presided. Mr. William B. Bell, President of the American Cyanamid Company, and Dr. E. C. Williams, Director of Research and Vice-President of the Shell Development Company, talked on the subject, "The Executive and the Technologist."

**• MERGE WITH U. S. TESTING**

The United States Testing Company, Inc. announced today the merger of the personnel and facilities of the E. E. Free Laboratories with the Testing Company. Dr. E. E. Free, before his death last November, was very active and well-known in many fields of scientific testing and research. He operated laboratories specializing in acoustics, light, electronics, vibration control and general physics. The E. E. Free Laboratories have played an important part in many new developments in engineering, and the merger with the Testing Company will permit the rendering of even greater services in the fields of testing and research.

The complete equipment, staff and associates of the E. E. Free Laboratories will be maintained at their present location—175 Fifth Avenue, corner of 23rd Street, New York. Mr. Douty, President of the United States Testing Company, Inc., points out that Mr. E. A. Graham, formerly associated with Dr. Free, will manage the laboratories which will be known as the Engineering and Research Division of the Testing Company.

**• "AVISCO"**

The name "AVISCO," registered in the U. S. Patent Office, has been established to designate Strong FIBRO, viscose rayon

staple fiber manufactured by American Viscose Corporation.

This special product is now in quantity production at the Nitro, W. Va., plant of American Viscose Corporation, where various types are being produced to meet the demand for as strong spun rayon yarns as possible, and to enable the fabric manufacturer to give the consumer increased serviceability in spun rayon garments. It is stated that it also enables the spinner to manufacture sizes not possible with standard staple production, and increases the number of possible uses for spun rayon.

### • JOINS ARIDYE

Clovis S. Powell, formerly superintendent of the Ware Shoals Bleachery, and for 28 years connected with that firm, has joined the Aridye Corporation. He will be connected with the Greenville, N. C., office of that organization.

### • COAL-TAR DYE EXPORTS

Exports of American-made coal-tar dyes, stains, and color lakes established a new record in 1939, with shipments aggregating 13,716,000 pounds valued at $6,432,000. During the preceding year exports of such products aggregated 8,575,600 pounds valued at $3,825,000.

While gains were gradual during the first eight months of the year, the large increase occurred following the outbreak of war in Europe.

### • KELCO SALES MEETING

To get away from the Northern snows, rains and unsettled weather, Kelco Company, makers of the Sodium Alginate thickening agent for printing pastes and discharge work, decided to hold their early Spring Sales Managers' meeting in Dallas, Texas.

The meeting was held on February 22 to February 24, under the direction of W. R. Kiely, General Sales Manager. Others present were D. E. Clark, Technical Director, with headquarters at San Diego, Calif.; H. T. Raup, Sales Manager, Pacific Coast Division, with headquarters at Los Angeles; R. O. Davison, Sales Manager, Central Division, with headquarters at Chicago, and Al Kleerup, Sales Manager, Eastern Division, with headquarters at New York City. Mr. Kleerup flew to Dallas from Jacksonville, Florida, after two weeks covering the East, Central and Southern Districts.

Sales plans and policies for the year 1940 were discussed.

### • NEW DYEING MACHINE

Methods of fabricating Stainless Steel have been developed by the Rodney Hunt Machine Company of Orange, Massachusetts, to a point where they were recently able to build a "Tru-Shade" Dyeing

Machine that was 20 feet long and of 6,000 gallon capacity. This is the largest Stainless Steel Dyeing Machine that has ever been built.

A dyeing machine of this size is made possible by a unique method of construction, patented by the Rodney Hunt Company which they call the "Curve-of-Strength" construction. By this method the sides of the tub have a natural bulge instead of the conventional square construction. They claim that the sides of a dyeing machine built of this construction will not buckle or flex under the tremendous pressure created by the dye liquor.

This particular "Tru-Shade" Dyeing Machine has been purchased from the Rodney Hunt Company by the Botany Worsted Mills. It is stated that, due to its tremendous size, they will be able to dye between 30 and 50 pieces at one time and obtain a perfect matching of color. While their 20 foot machine is the largest unit to date, the entire Botany Dyehouse has been modernized with "Tru-Shade" equipment.

Another engineering feat that is of interest in connection with this machine was the design and construction of one of the longest Stainless Steel Reels ever built. This Reel is 20 feet long and entirely unsupported by any middle bearings. To make it possible to build such a Reel, the Rodney Hunt Company has invented and patented a new "pipe body" type of construction.

The shipment of this "world's largest" Dyeing Machine culminates one of the most successful years in the history of the Rodney Hunt Machine Company. The company states that during this past year they have built and installed "Tru-Shade" Stainless Steel Dyeing Machines for many of the largest and best known mills in this country and Canada.

### • CHEMISTS ALUMNI ASSN.

Dr. Donald Price, chief research chemist for the National Oil Products Co., Harrison, N. J., recently was elected president of the newly organized Chemists' Alumni Association of Columbia University, New York City.

Dr. Harry L. Fisher, associate director of research, U. S. Industrial Alcohol Co., was elected vice-president, and Wendell G. Fogg, chief chemist of Air Reduction Co., Stamford, Conn., secretary-treasurer. Election of officers was held at the January meeting, but the announcement was withheld until all alumni were notified.

Dr. Price has been associated with the National Oil Products Co. for 3½ years, starting as a chemist in the research laboratory.

### • FORD EXHIBIT, N.Y.W.F.

So popular was the display of Shelton Looms in the Ford Exposition at the New York World's Fair last summer, that this textile manufacturer will show several additional processes in the making of automobile upholstery in its enlarged exhibit at the 1940 Fair.

The entire story of automobile upholstery from the carding of raw cotton, through the spinning of yarn and the weaving of cloth will be graphically displayed. Three new machines are being added to this Exhibit—a drawing frame, a roving frame and a spinning frame. Thus, the actual spinning of yarn will be shown this year for the first time. Last season only carding and weaving were shown.

The exhibit has been assigned a new location near the entrance of Industrial Hall where it will occupy nearly twice as much space as in 1939. Already, the looms have been moved and installation in their new exhibit island is proceeding rapidly.

### • CALCOLOID PIGMENT DYEING METHOD

Announcement has been made by Calco Chemical Division of American Cyanamid Company of the Calcoloid Pigment Dyeing Method which is entirely new, and different than any other method. It is said among other things to be the only process by which cross overs and other costly difficulties are entirely eliminated in package dyeing.

For more than a year several large mills have cooperated with Calco, and it is claimed that in actual operation demonstrated that the Calcoloid Method gives full penetration, with attendant level dyeing, more certain and uniform shade matching, and maximum fastness to washing and crocking.

It is said that evidence of remarkable level dyeing is furnished by Recording Photo-Electric Spectrometer graphs of a test sock, knit with yarn taken from the outside, middle, and inside of the spool. Such a test with other methods shows distinct shade variations, and white cross overs. In this case the three Spectrometer curves come so close as to look like one.

Another important advantage of this method is that more yarn can be wound on a spool, permitting the dyeing of more yarn at a time. In connection with this improved dyeing method Calco has also perfected the dyes themselves so that Calcoloids, specially processed for the method,

are now said to be extremely fine and highly dispersible. They are patented, and patents are pending covering the Calcoloid Pigment Dyeing Method.

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### • ANNUAL STYLE SHOW

Dr. Thomas Nelson, Dean of the Textile School of North Carolina State College, announced recently that the home economics departments of ten North Carolina colleges for women had accepted the invitation to cooperate with the Textile School and participate in the annual Style Show which will be held at Raleigh on April 25th. The cooperating institutions are Appalachian State Teachers College, Boone; Elon College, Elon; Flora Macdonald College, Red Springs; Greensboro College, Greensboro; High Point College, High Point; Louisburg College, Louisburg; Meredith College, Raleigh; Peace Junior College, Raleigh; Queens College, Charlotte; and Saint Mary's School, Raleigh.

At that time more than 100 young women who are studying home economics in the cooperating institutions will model costumes which they have made as a part of their regular classroom work from fabrics designed and woven at State College by Textile students.

In 1928, when the women of America had become more or less silk-minded, Dr. Nelson conceived the idea of creating consumer interest in cotton and rayon products by having college girls demonstrate the attractive costumes which could be made from such materials. Miss Ellen Brewer, head of the home economics department of Meredith College, agreed to cooperate with the Textile School and the agreement was sanctioned by Dr. C. E. Brewer, then president of Meredith.

Since that time more than one thousand home economics students whose homes were in many states have participated in the State College Style Show and have demonstrated to thousands of visitors that the cotton and rayon fabrics designed and woven at State College can be made into costumes of utility and beauty. Many of the young women who took part in the Style Shows of previous years are now teachers in high schools and are transmitting their enthusiasm for cotton and rayon products to the students in their classes. These Style Shows in addition to helping revive consumer interest in these products, have also shown the high caliber of work done by young women in the home economics departments of North Carolina colleges for women, and by Textile students at State College. Since its inception 14 colleges have cooperated with the Textile School in staging this Style Show.

# • OPEN FORUM •

**Rules under which this department of the REPORTER is conducted are as follows:**

**1. Anyone who has a technical problem on which he would like advice may submit it to the Reporter and it will be published in the first available issue.**

**2. Any reader who feels that he has a solution of the problem may forward his reply to us and if we feel that the reply is suitable it will be published in a succeeding issue.**

**3. For each such reply published the Reporter will pay a minimum of $2.**

**4. In case there is more than one answer to the same question, the one covering the subject in the most complete and authentic manner will be published, or if two answers are sufficiently different both will be published. If two answers are considered equally good, the one first received will be given priority.**

**5. The Reporter will assume no responsibility whatsoever for the accuracy of the answers submitted—it is simply offering a vehicle for the public expression of its readers' opinions.**

**6. Both the questioner and answerer must send in his complete name and address. When requested we will publish only the initials or other identifying insignia.**

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## New Question

49—I would appreciate obtaining a list of fugitive stains for wool, cotton, silk, viscose and acetate rayons to be used on any of these or combinations of them.

Yarns are to be steamed 15 minutes at 210° F. before weaving into dress goods, stains to be removed by normal finishing.—**L. C. G.**

## Answers

47—In recent months we have experienced an entirely new trouble, the very uneven package dyeing of several lots of mercerized yarns, both high grade Combed Peeler and Sak, and both warp and skein mercerized. Satisfactory formulas and methods in the same dyeing machines on the same day act entirely differently on different lots of yarn, therefore methods or water or machines or dyestuffs are not responsible. The dyeing is uneven and the shade is entirely off. On the worst yarn lots there is an actual precipitate from the dyestuff on the outside of the packages. The dyeing is direct, also developed. The worst yarn is also troublesome in skein Vat Dyeing, not in unevenness but in consuming 20 per cent too much dyestuff. The yarn which dyes unevenly with direct dyes in packages can be dyed nearly evenly in skeins with special care. The package dyeing is done in the original wetting out bath and no betterment when the yarn is separately boiled out with scouring or soluble oil. None of the troublesome yarn shows an alkaline reaction from imperfect souring but in some cases a slight souring before dyeing has helped and in other cases no. We notice the most troublesome yarn takes many times as long to wet out in the standard laboratory wetting out test as the satisfactory yarn but in the uneven dyeing we are sure the yarn was properly wet out. In other words the troublesome yarn seems to be to a certain extent waterproofed and to have a precipitating effect on dyestuffs. There are certain chemicals used on Cotton, which are permanently absorbed by cotton and which produce results identical with the above, but the spinners say they use no chemicals whatever and the mercerizers use only caustic and proper souring procedure. What do you say is wrong with the troublesome lots of mercerized yarns and can you suggest remedies? **G.L.**

**Answer No. 4**—I have read with interest in your Forum, Question No. 47, relative to streaky dyeing, mercerized yarns; Peeler and SAK qualities. A few years back we had the same problem and practically everything given in answer so far was tried, even the kier boiling and bleaching of these faulty yarns, which did improve results but not overcoming them completely.

Examining these faulty yarns under a microscope, we found that the parts of thread dyeing lighter by approximately 20 to 25 per cent, were more shiny, appeared strained and were out of round. The darker

sections of the thread were round and darker, appearing bronzy but were most likely the natural shade expected. These sections were a marked contrast to the lighter sections.

We finally found that the warp mercerizer had increased tension on his range to get more luster to meet competition, which tension was apparently not uniform and caused the trouble. We had to convert this yarn into black and white where the difference even there showed up considerably. In the black we found it required approximately 25 per cent more color than our normal shade of black. And the white still carried shiny, glossy places where the thread was out of round. It appears that the complainant should take his problem up with the mercerizer, having ferreted out all possibilities of fault under his jurisdiction.—**W. D. L.**

**48**—One of our correspondents presented the following problem. We hope that some of our readers will be able to give the necessary information.

"Our black shades and some of the very dark blue, after dyeing are given a treatment we call 'painting,' which consists of running the cloth over a knurled roller, the roller turning in a bath of the pigment solution with the surplus being scraped off with a doctor blade. The solution consists of ground Prussian Blue with turpentine and linseed oil, the proportions being on the average about six pounds of Prussian Blue, ten pounds of turpentine and 100 pounds of linseed oil.

"The amount picked from the roller by the cloth is then thoroughly brushed into the cloth, after which the cloth has to be cured or 'stoved.' This consists of hanging the cloth in festoons in large chambers which are then closed and heated to approximately 250° F. The cloth must stay in these chambers a minimum of twelve hours, and in some cases where the 'painting' solution is somewhat heavier than average, twenty-four hours is required for proper drying and oxidation.

"We know that there are mechanical dryers on the market which will give better heat and considerably better circulation than we now have in our stoves thereby shortening the curing time considerably, but we believe the better solution is from some chemical means of quicker drying through oxidizing materials."—**L. B. B.**

**Answer**—Your correspondent on the above problem has asked for information concerning chemical means for hastening the drying of linseed oil, Prussian Blue and turpentine mix when applied and brushed into cloth.

While I would not attempt to give a definite answer to the problem, I do believe I can give enough suggestions so that the writer can solve the difficulty himself.

In the first place, as long as not mentioned otherwise, I assume the linseed oil used is raw. I would suggest that he look into the possibilities of a processed or bodied linseed oil—one which I would suggest is ADM-100 oil manufactured by Archer Daniels Midland Co.

Secondly, I would suggest he try using instead of turpentine (unless it must be used) one of the various so-called mineral spirits such as Varsol (Socony), Solvesso (Standard Oil of N. J.) or Sunoco Spirits (Sun Oil Co.)

Lastly, I would suggest he write Nuodex Products, Inc., Elizabeth, N. J., and state the drying problem, telling whether he is using raw or bodied oil and ask their advice. This company manufactures chemically correct solutions of metallic driers. They also publish technical bulletins and charts which are very helpful. Technical Bulletin No. 8, August, 1934, makes definite suggestions as to what driers to use and how much to dry raw linseed oil.

The reason I suggest that your correspondent try ADM-100 processed oil is that such an oil dries more quickly than a raw oil even though no outside drier is added. The reason for using mineral spirits instead of turpentine is that the former is cheaper and evaporates more rapidly.

I know the above information is reliable from actual experience and hope it helps solve the problem for the person interested.—**William B. Robinson.**


## • CLASSIFIED ADVERTISEMENTS •

**The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.**

WANTED: Textile Chemist: Opening for recent graduate with one or two years experience in textile finishing or printing, for laboratory and technical sales work. Write Box No. 233, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.

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